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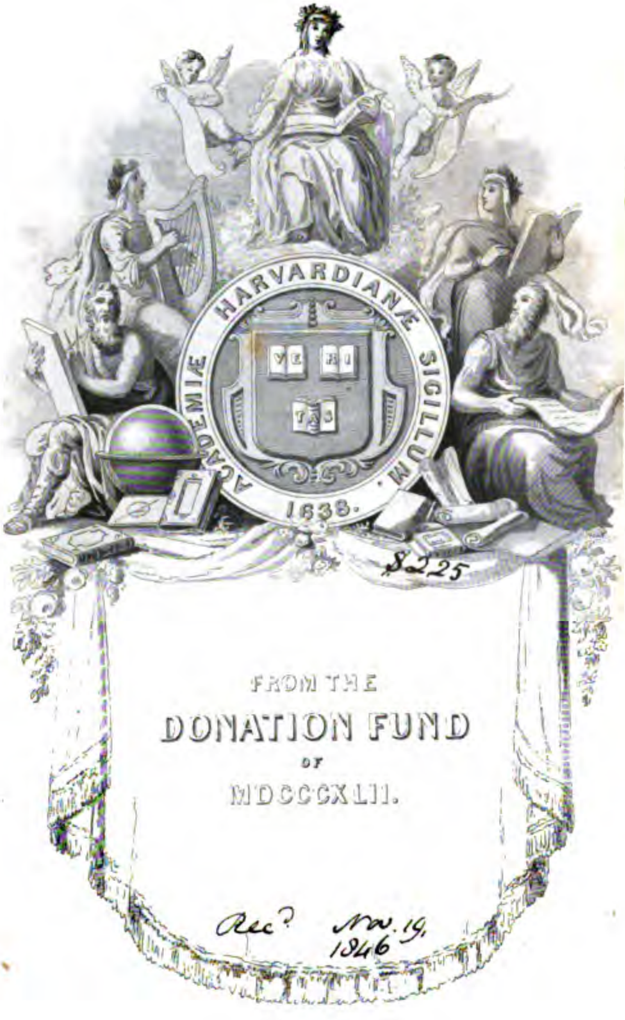

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OF

CHEMISTRY,

INCLUDING THE APPLICATIONS OF THE SCIENCE IN THE ARTS.

BY

THOMAS GRAHAM, F.R.S. L. & Ed.

PROFESSOR OF CHEMISTRY IN UNIVERSITY COLLEGE, LONDON; PRESIDENT OF THE CHEMICAL SOCIETY; CORRESPONDING MEMBER OF THE ROYAL ACADEMIES OF SCIENCES OF BERLIN AND MUNICH, &c.

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PREFACE.

The important bearings of the laws of heat, particularly in reference to the physical condition of matter, have led to their consideration before the chemical properties of substances, in this as in most other elementary treatises on chemistry. Light is then shortly considered, chiefly in reference to its chemical relations. The principles of its Nomenclature, in which compared with many sciences, chemistry has been highly fortunate, are then explained, together with the Symbolical Notation in use, by means of which the composition of highly compound bodies is expressed with the same palpable distinctness, which in arithmetic attends the use of figures, in place of words, for the expression of numerical sums.

A considerable section of the work is then devoted to the consideration of the fundamental doctrines of chemistry, under the heads of Combining Proportions, Atomic Theory, Doctrine of Volumes, Isomorphism, Isomerism, Constitution of Salts, and Chemical Affinity, including the propagation of this action through metallic and saline media, in the voltaic circle.

The materials of the Inorganic world are then described, under the two divisions of non-metallic elements and their compounds, and metallic elements and their compounds.

Lastly, the numerous compounds of the Organic world are discussed. In this department, a most extraordinary progress has been made within a very short period. The study of organic chemistry has also been much facilitated by classification, and the arrangement under Compound Radicals, introduced by M. Liebig.

It was now obvious that the science was sufficiently advanced to be applied to the elucidation of the great questions of vegetable and animal physiology. A condensed view is given of the new discoveries in the former department, and also of the important conclusions respecting the animal functions of respiration and digestion, results which are entirely new, and now enter for the first time into a systematic work on Chemistry.

University College,
November, 1841.

ERRATA.

Page 22, line 18, *for* iron melts *read* cast iron melts .

.. 55, in table *for* temperature 242° *read* 212°

.. 59, in figure 3, introduce *d* in the upper circle, and *f* in the lower square

.. 61, in the figure, the tubes should be represented not open, but closed at the top

. 120, second line from bottom *for* 1895.5 *read* 1894.5

.. 121, lines 18 and 19, *for* 1294.5 and 1795.5 *read* 1394.5 and 1895.5

.. 130, in the diagram representing the combining measure of chlorine *for* 1269.5 inscribed in each square *inscribe* 2470

.. 134, 9 lines from bottom *for* choloroform *read* chloroform

.. 149, line 13, *for* Fe_2O_3 *read* FeO,SO_3

.. 155, line 16, *for* similarity of form *read* similarity of composition

.. 177, line 21, *for* Ag *read* Hg

.. 202, in figure 4, transpose the terms austral pole and boreal pole

.. 210, in figure 12, *insert* F at the top and A at the bottom of the semicircle

.. 290, line 7 from bottom, *for* 1039 × 34, *read* 1039.3 × 4

.. 296, line 6, *for* best soluble *read* least soluble

.. 312, line 13, *for* SiO_2, *read* Si

.. 314, line 16, *dele* be

.. 322, to table of sulphurous acid series, add :

Crystals of the leaden chambers (de la Provostaye)	$SO_2 + Cl + SO_2O$
Oxichloride of sulphur (H. Rose) . . .	$SO_2 + Cl + SO_2O$

.. 330, line 10 from bottom, *for* Herschell *read* Herschel

.. 336, line 15, *for* hyposulphite *read* hyposulphate

.. 362, in table of chlorides, *for* hypochorus *read* hypochlorous

.. 390, line 8, for iodate *read* iodite

.. 405, line 12 from bottom, *for seleniuretted read selenietted*

.. 424, line 17 from bottom, *for* half *read* twice

.. 468, line 6, *for* 11 times *read* 5½ times

.. 471, line 8, *for* 12,000 tons *read* 40,000 tons

.. 478, line 18, after not efflorescent *dele* when free from carbonate, *and insert* although injured by acid fumes

.. 596, line 1, *for* Pattenson *read* Pattinson

.. 618, line 1, *for* $Na + O2WO_2$ *read* $NaO + 2WO_2$

.. 652, line 13, *for* chloride of strontium *read* bromide of strontium

.. 684, line 13, *for* hydrochlorate *read* chloride

.. 927, line 9 from bottom, *for* vegetables *read* nutgalls

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PART III.

ORGANIC CHEMISTRY.

CHAPTER I.

SECTION I.

PRELIMINARY OBSERVATIONS.

By organic substances are meant definite chemical compounds, found ready formed in organized beings, and their modifications produced by artificial processes which may be greatly varied. These substances are known to be definite in composition when they are crystallizable, or when they enter into compounds that are crystallizable; or have, if liquid, a fixed boiling point. In their number, which has been vastly increased by late researches, are found many acids, several alkaline bodies, and a large class of neutral substances which cannot be assimilated to any class of inorganic compounds. Recent inquiries have disclosed some unexpected relations between different organic substances, and supplied the means of associating groups of them from similarity of composition. There is the same evidence of the existence in these substances of compound radicals, which may be transferred from a state of combination with one element to another, as in the compounds of the inorganic kingdom allowed to contain such constituents; although the organic radicals cannot be isolated and exhibited in a separate state, except perhaps in a single instance. The radicals most characteristic of organic compounds, hitherto investigated, are of the basyle class, bodies resembling therefore the metallic elements in their functions and the series of compounds with salt radicals which they are capable of forming. Of all these hypothetical radicals ammonium has served as the prototype; they are allowed however to differ in one respect from ammonium and the metals, namely in combining readily with hydrogen, which element acts towards them as a salt-radical. The supposed prevalence of such radicals in the constitution of organic compounds has led M. Liebig to define organic chemistry as *the chemistry of compound radicals;* the whole of which indeed as are of a basyle character, including ammonium itself, may be properly assigned to this department of the science.

Many organic substances are highly complex and contain a large number of atoms; a circumstance which renders them very liable to change, and has led to the observation of peculiar modes of decomposition among organic compounds, indicating novel modes of the action of chemical affinity.

COMPOSITION OF ORGANIC SUBSTANCES, AND METHOD OF ANALYSIS.

The elements which usually enter into organic substances are few in number, namely carbon, hydrogen, oxygen and nitrogen. Some organic substances contain only carbon and hydrogen, as olefiant gas and other hydro-carbons; more frequently carbon, hydrogen and oxygen, as sugar, gum, many neutral bodies, and most organic acids. To these a fourth element is added, nitrogen, in the vegeto-alkalies and various other compounds which belong more usually to the animal than vegetable division; indeed carbon prevails in the organic world, as silicon does in the mineral, and as most minerals are silicates, so organic substances are the compounds of carbon. To these elements certain others are occasionally added, although most usually by artificial processes, as chlorine in the place of hydrogen, and sulphur, phosphorus, arsenic or tellurium in that of oxygen. The elementary analysis of organic matters is determined with much exactness, and by means so simple and rapid of execution as to render an ultimate analysis often the most ready test of the purity of a substance. The process followed, consists in burning the matter to be analysed by means of oxide of copper, so as to convert its carbon into carbonic acid and its hydrogen into water, which are both collected and weighed; when the matter contains nitrogen, the latter is collected in the form of gas. The oxygen, which the matter contains, is represented by the excess of its weight over the sum of the weights of the carbon, hydrogen and nitrogen found. I shall merely sketch the outline of this fundamental and highly important process, referring for the minute instructions necessary for its exact execution to Professor Liebig's valuable tract on Organic Analysis.*

The nitrate of copper, decomposed by a red heat in an earthenware crucible, gives a fine light oxide, very suitable for the combustion process, and of which a considerable quantity must be provided. It is a property of this oxide to be reduced with extreme facility at a red heat, by carbon or hydrogen, and at the same time to resist an intense temperature, when heated apart from combustible matter, without losing a particle of oxygen. The substance to be analysed, or burnt with oxide of copper, we shall suppose to be sugar.

The tube for combustion is of the most difficultly fusible glass, free from lead; no variety answers better for it than the white Bohemian glass. It is generally about 0.4 inch in internal diameter, and 14 or 15 inches long, drawn out, bent and sealed at one end, as represented (Figure 85,) and open at the other. To have some measure of the quantity of oxide of copper to mix with the substance to be analysed, the tube is to be filled to three fourths of its length with pure oxide of copper, out of a crucible in which it has just been ignited, and while it is yet warm. From 5 to 7 grains of dry loaf sugar in fine powder are first rubbed in a porcelain mortar with a little oxide, with which it is intimately mixed, and by degrees the whole oxide of copper is added, which was measured in the tube. Having first introduced pure oxide of copper, so as to fill about half an inch at the closed end of the tube, the mixture from the mortar is then introduced, followed by a portion of oxide employed to rinse out the mortar, and the last covered by pure oxide, so as to fill up the tube to within one inch of

FIG. 85.

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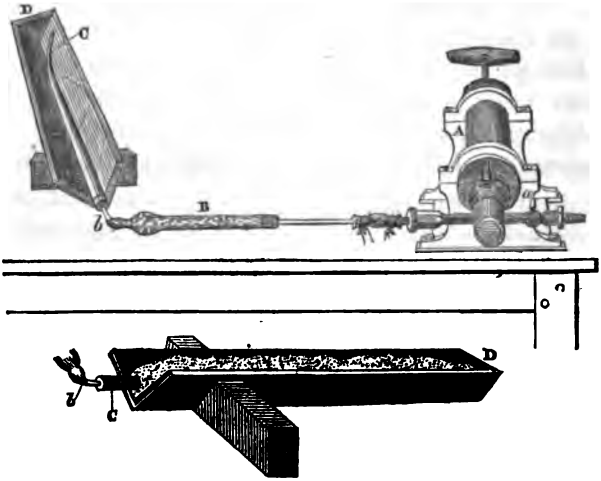
* Translated by Dr. W. Gregory, and forming Part I of Griffin's Scientific Miscellany. Tegg, London.

its open extremity. The lengths occupied by the different layers of pure oxide, mixture, rinsings of mortar and again pure oxide are indicated by dotted lines in the figure. The weight of the whole oxide of copper used generally exceeds 1200 grains.

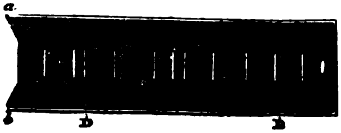
In these operations, the oxide of copper inevitably absorbs a quantity of moisture from the air, which may amount to 0.2 or 0.3 grain, and which coming off afterwards during the ignition would vitiate the determination of the hydrogen. The tube and oxide must therefore be dried by a heat which will not decompose the sugar. This is done by placing the combustion tube C, in a wooden trough D, (Fig. 86) and covering it with sand of the temperature of 250°; connecting it at the same time by a perforated cork *b*, with a tube B, containing fragments of chloride of calcium, and an exhausting syringe A. By means of the latter, air and moisture are withdrawn from the combustion tube, the moisture being retained by the chloride of calcium in B; air is then admitted to C by the stopcock *a*, and withdrawn again by the syringe ten or twelve times. The mixture may then be considered dry.

Fig. 86.



The furnace for the combustion is made of sheet iron of a

FIG. 87.



trough form (Fig. 87), 22 to 24 inches long and 3 inches high. The bottom is 3 inches wide, with narrow apertures about half an inch apart, which form a sort of grate; the sides of the furnace are inclined outwards, and 4½ inches apart at top. To support the combustion tube, pieces of strong sheet iron of the form D, (Fig. 88), are rivetted to the bottom of the furnace, at intervals; they are of exactly equal height, with their edges ground flat, and correspond with the round aperture in the front of the furnace, A. The furnace rests upon two thin bricks supported upon two blocks of wood, which are separated a little by a wedge, so as to elevate slightly the further end of the furnace as in Fig. 89.

FIG. 88.

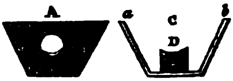
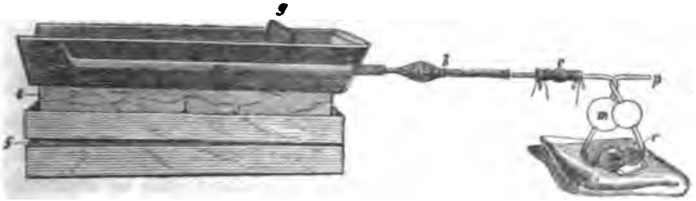


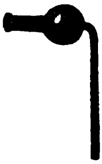
FIG. 89



When the heat is to be increased, the furnace is raised a little on one side, by a thin bit of tile placed below. Good charcoal, is the fuel employed in this furnace; the combustion may be animated by fanning the burning embers with a square piece of pasteboard; which is safer than raising the furnace off the bricks. Immediately connected with the combustion tube, by means of a perforated cork, is a tube of the form *b* (Fig. 89), containing fragments of strongly dried, but not fused chloride of calcium. In this tube is condensed the water formed in the combustion, of which the weight is ascertained by weighing the tube, before and after the combustion. Beyond the chloride of calcium tube and connected with it by a short caoutchouc tube, *c*, is a glass instrument *p m r*, containing a strong solution of caustic potash, of density 1.25 to 1.27, for the absorption of the carbonic acid produced in the combustion, This instrument consists of five balls, of which *m* is larger than the others; no more of the potash ley is put into it than fills the three central bulbs, leaving a bubble of air in each. One corner is elevated a little by a cork placed under it, and the whole supported upon a folded towel; the potash apparatus, when filled with ley, commonly weighs from 750 to 900 grains. This apparatus is also weighed before and after the combustion, and the increase ascertained.

Before introducing the combustion tube into the furnace, it must be tapped smartly in a horizontal position, so as to produce a vacant space above the oxide of copper through the whole length of the tube, by which the gaseous products may escape (Fig. 85). The same precaution must be taken in the preparatory operation of drying the oxide of copper, otherwise it often happens that a portion of the oxide is thrown forwards out of the tube. Before beginning the combustion, it is necessary to ascertain that all the joinings are tight, by sucking out a bubble or two of air from the apparatus, by means of the suction tube (Fig. 90), applied by means of a perforated cork not fitting very tightly to the open end of the potash apparatus. The slight exhaustion causes the ley to stand 1½ or 2 inches higher in the inner limb *m* of the potash apparatus than in the outer limb. This elevation will be maintained if no air enters by the cork or caoutchouc joint, and the apparatus is then certainly tight, but not so if the level changes and the liquid falls back into the middle part of the apparatus.

FIG. 90.



In conducting the combustion, the anterior portion of the tube, containing only oxide of copper, is first surrounded by red hot charcoal. The fragments of charcoal are kept in their place and the heat prevented from spreading, by a screen, (Fig. 91) of sheet iron, of the same width as the furnace. This screen is slowly moved backwards, by half an inch to an inch at a time, and the fire space immediately filled up with red hot charcoal, so as to raise rapidly the portion of tube newly exposed to a red heat. A screen (Fig. 92) should be placed upon the front

FIG. 91.

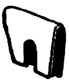
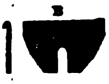


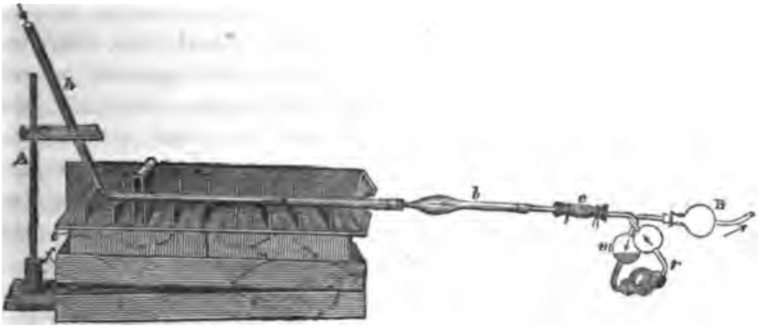
FIG. 92.



of the furnace, to prevent the cork being burned and the chloride of calcium tube being heated, by radiation from the furnace. But the fore end of the tube, which is empty and projects an inch beyond the furnace, should be kept so hot during the whole operation that no water condenses in it; in the course of twenty minutes or half an hour the screen has been moved to the end of the tube, and the combustion completed. When the evolution of gas stops all at once, the combustion is certainly complete, and a good result is obtained; the tube should be heated red hot, but not to bright redness; it begins to stick to the supports when heated too hot.

As soon as the evolution of gas terminates, the potash ley begins to rise into the bulb *m*. The pointed extremity of the combustion tube should then be broken by means of a pair of pliers, after removing the charcoal from that end of the furnace. An open tube *h*, 12 or 15 inches long, is then placed over the opened end, and supported by a stand, (Fig. 93), while by means of the suction tube B, a certain quantity of air is drawn by the mouth through the potash apparatus. The whole watery vapour and carbonic acid remaining in the combustion tube, are thus brought into the chloride of calcium tube and potash apparatus, and completely absorbed.

FIG. 93.



The data furnished by the combustion afford the means of calculating the composition of the substance analysed, as the composition of water and carbonic acid is known, the former consisting of 1 hydrogen and 8 oxygen in 9 parts, and the latter of 27.675 carbon and 72.325 oxygen in 100 parts:

The hydrogen is one ninth of the increase of weight in the chloride of calcium tube.

The carbon is 27.67 per cent of the increase of weight in the potash bulbs.

The oxygen is the quantity obtained by adding the weights of the hydrogen and carbon together, and deducting their sum from the weight of matter originally employed.

The following are the details of a particular analysis of sugar (Dumas).

Weight of Sugar. . . .	600
Weight of Carbonic Acid.	921
Weight of Water. . . .	353

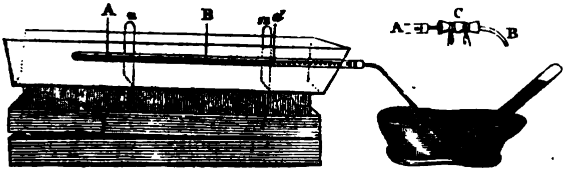
These give by calculation :—

Carbon.	254.6	42.4
Hydrogen. . . .	39.2	6.5
Oxygen.	306.2	51.1
	600	100

The atomic constitution of sugar is obtained from these results, by dividing the quantities of carbon, hydrogen and oxygen in the last column, by their equivalents, 76, 12.5 and 100. We thus obtain 0.558 of an equivalent of carbon, 0.520 of an equivalent of hydrogen and 0.511 of an equivalent of oxygen, which are more nearly proportional to the following than any other whole numbers, 12 carbon, 11 hydrogen, 11 oxygen; and give $C_{12}H_{11}O_{11}$, the usually received formula for cane sugar.

The estimation of nitrogen, when present in an organic substance, requires another combustion in which that gas is determined by measurement. This gas generally escapes in a free state, mixed with the carbonic acid and watery vapour; but frequently deutoxide of nitrogen is formed, which renders the determination of the nitrogen difficult; to decompose the latter it is necessary to have a portion of copper turnings in the anterior part of the tube, which are kept at a full red heat during the combustion, as from the screen *m* (Fig. 94) to the mouth of the tube. This is followed by a layer of pure oxide from *m* to B, and then the mixture from B to A; as soon as the copper

FIG. 94.



and oxide are at a red heat, the tube is heated from the closed end, a second screen *n* being gradually advanced from that extremity. When the proportion of nitrogen is not inconsiderable, it is generally sufficient to determine its relation by volume to the carbonic acid evolved at the same time. This is done by attaching a bent quill tube (Fig. 94) to the mouth of the combustion tube, by which the gas evolved is conveyed to the mercurial trough, and collected at different stages of the combustion in a small graduated jar. By passing up a few drops of caustic potash into the gas in the jar, the carbonic acid is absorbed and the nitrogen remains. If the proportion between the volumes of the two gases thus observed is the same in several successive trials, and no red nitrous fumes be perceived on mixing the gas with air, this result is sufficient for the nitrogen. The whole quantity of carbonic acid produced in the combustion being known from a previous analysis conducted in the usual way, we can obtain the volume of nitrogen by calculation, and thence its weight. Or, as two volumes of carbonic acid and of nitrogen represent both one atom of carbon and nitrogen, the atoms of these two gases are in the same number as the volumes observed; consequently when the weight of the carbonic acid is known, that of the nitrogen may be calculated from the atomic weights of carbonic acid and nitrogen.

For the analysis of uric acid, in which the volumes of the nitrogen and carbonic collected are as 4 to 10, and of bitartrate of ammonia in which they are as 1 to 8, this method answers very well, but when the proportion of nitrogen is smaller than the last, or when the nitrogen appears in a variable proportion at different stages of the analysis, then it is necessary to collect and measure the whole nitrogen evolved, which is not easily done with accuracy. To get rid of the nitrogen of the air contained in the tube, a combustion tube is chosen 24 inches long, 6 inches of which at the closed end are filled with carbonate of copper, then follow 2 inches of pure oxide of copper, next the mixture of the substance with oxide of copper, then another layer of pure oxide, and lastly a layer of copper turnings. The air is exhausted from the tube by a syringe, and the tube filled with carbonic acid by heating one half of the carbonate of copper; the exhaustion and evolution of carbonic acid are several times repeated, till the whole air is certainly withdrawn from the tube, and the latter is filled with carbonic acid. The combustion of the mixture is then conducted as in the previous case, the gases however are received in a large graduated jar, over mercury, half full of a strong solution of caustic potash. After the combustion is completed, heat is again applied to the end of the tube containing the remaining half of the carbonate of copper, and carbonic acid evolved which sweeps out the last portions of nitrogen into the receiver, where the volume of that gas is observed.

MM. Will and Varrentrapp have lately proposed the following excellent method of determining the nitrogen in organic substances, which is likely to supersede every other. The substance is mingled with a mixture of caustic lime and hydrate of soda, and heated to redness in a combustion tube. All the nitrogen of the substance escapes as pure ammonia, which may be condensed in a small apparatus containing dilute hydrochloric acid. This liquid is afterwards mixed with chloride of platinum, and brought to dryness in a water-bath; the double chloride of platinum and ammonium remaining is washed with a mixture of alcohol and ether, in which it is perfectly insoluble. The quantity of nitrogen is calculated from the weight of the chloride of platinum and ammonium, or from the metallic platinum which it leaves behind when heated to redness.

Oxide of copper is not applicable for the combustion of substances containing chlorine, owing to the volatility of the chloride of copper, a portion of which passes into the chloride of calcium tube, and vitiates the determination of the hydrogen. Chromate of lead is then employed in the combustion tube, with the same manipulations as with oxide of copper. This salt must first be strongly ignited till it begins to melt and then be reduced to a very fine powder; the chloride of lead is perfectly fixed at a low red heat. The chromate of lead is not in the slightest degree hygroscopic, and is likely to be preferred to oxide of copper, where it is desirable to determine the proportion of hydrogen with extreme accuracy.

Notwithstanding the great value of the analytical results of this method, and the agreement almost perfect in repetitions of the same analysis, there can be little doubt that the method itself is not absolutely exact. From the rigorous examination to which the combustion process has lately been submitted by M. Dumas, it appears to give less than the true quantity of carbon. The loss of carbon is ascribed to several causes: some is deposited here and there in the tubes and for want of oxygen not burned; the reduced copper is partly converted into carburet of copper; the liquid potash allows a portion of the carbonic acid to escape, and lastly the air which is drawn through the apparatus takes up some water from the same potash and diminishes its weight. This loss of carbon was hitherto concealed by carbonic acid being allowed to contain more carbon than it really has, so that the carbon lost in the process was made up in the calculation; and the formulæ deduced from analyses are only true from the accidental compensation of these two errors. Dumas reduces the proportion of carbon in carbonic acid from 27.67 to 27.27 per cent, and obtains for the atom of that element the number 75, instead of 76.4. This important result he has deduced by collecting and weighing the carbonic acid produced by the combustion of a known weight of pure charcoal, in the forms of graphite and the diamond.* Drs. Marchand and Erdman of Berlin have repeated these analyses with the same results; it is now indeed generally allowed that the atomic weight of carbon of Berzelius is too high, but chemists are not yet agreed as to the amouut of reduction to be made. MM. Redtenbacher and Liebig conclude that the atomic weight of carbon is the intermediate number 75.854, from an elaborate series of experiments undertaken to determine the point, in which the proportion of silver in the acetate, malate, racemate and tartrate of that base was ascertained with great accuracy; the atomic weight of silver, respecting which there is little uncertainty, being taken at 1351.6. It has also been shewn by Dr. Clark that when certain corrections are made on the calculations of Berzelius' experiments, they really give a number for carbon nearly approaching to this.

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* MM. Dumas and Stass, Annales de Chimie et de Physique, 3me. Série, tome 1, p. 5. (1841).

To give the process of organic analysis all the precision of which it is susceptible, M. Dumas requires attention to the following circumstances. 1. To triple at least the quantity of matter usually employed. 2. After the ignition of the combustion tube to pass through it a large quantity of oxygen, so as to burn the deposited carbon and re-oxidate all the copper, which gets rid of the carburet of copper. 3. For the reception of the water to employ a chloride of calcium tube accompanied by a tube filled with fragments of pumice impregnated with oil of vitriol. 4. To absorb the carbonic acid, Liebig's bulb apparatus containing solution of potash is to be used, accompanied by tubes containing potash moistened with the potash ley on one side, and dry potash on the other; the dry potash arrests the water with which the gas has become charged by passing through the liquid in the bulbs.* The most important observation of Dumas is that the combustion of the carbon is never complete, unless oxygen be passed through the tube containing the mixture of oxide of copper and matter to be analysed, and the matter be thus burned in an atmosphere of oxygen. This is the principle of the method of organic analysis originally practised by Dr. Prout, by which he was led to the conclusion that the atom of carbon is exactly 6 on the hydrogen scale, or 75 on the oxygen scale.‡ M. Dumas, who now adopts this conclusion, has therefore been conducted to it by a recurrence to Dr. Prout's own mode of investigation.

MODIFICATIONS OF ORGANIC COMPOUNDS PRODUCED BY ARTIFICIAL PROCESSES.

It is generally stated that no substances properly organic can be produced by directly uniting their ultimate elements; although a few organic compounds may be formed from substances less complex than themselves, but which are not elementary; as urea from cyanic acid and ammonia, the acid named, in common with cyanogen itself and all its compounds, being considered organic, because usually derived from the decomposition of azotised matters. But it has unequivocally been proved that nitrogen gas unites with charcoal under the influence of carbonate of potash at a red heat, and forms cyanide of potassium (L. Thompson, Fownes).* The last salt also yields ammonia when decomposed by water; so that cyanogen, and through cyanogen ammonia, can be primarily derived from their elements contained in the inorganic world. The usual course however pursued by the chemist in this department is to form new compounds by the alteration of compounds supplied to him by nature. These changes he effects by various agencies, such as hydrate of potash, distillation by heat, acids, oxygen, chlorine, &c. The most uniform and definite of these actions are those of a hydrated alkali and dry distillation.

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* Annales de Chimie et de Physique, 3me Série, tome 1, p. 39, where the improved process is minutely described and the apparatus figured.

‡ Phil. Trans. 1827; or Brande's Manual of Chemistry, p. 1060.

Distillation with an alkali.—When an organic substance containing no nitrogen is fused with a sufficient quantity of hydrate of potash, no charcoal is liberated. The products formed are those which result from oxidation; water is generally decomposed, of which the oxygen enters into combination with the hydrogen and carbon of the organic matter, while the hydrogen is disengaged as gas. Thus when acetate of soda is decomposed by hydrate of barytes, the hydrogen of the latter is liberated. M. Dumas has shewn that alcohol and other bodies of the same character, distilled at a moderate heat with a mixture of hydrate of potash and quicklime, each gives rise to a peculiar acid, which remains in combination with the potash, by losing 2 eq. of hydrogen (disengaged as gas), and acquiring 2 eq. of oxygen; alcohol to acetic acid, wood spirit to formic acid, fousel oil to valerianic acid, ethal to ethalic acid; and that this mode of decomposition is characteristic of alcohols. Glycerine, which in some respects resembles an alcohol, when treated in the same way, but at a very low temperature, does not give a peculiar glyceric acid, but resolves itself into acetic and formic acids, with the loss of two equivalents of hydrogen and assumption of two of oxygen. Acetone transmitted in the state of vapour over the mixture of hydrate of potash and lime heated to redness, gives nothing but carbonic acid, which remains in combination with the alkali, and light carburetted hydrogen C_2H_4. The vapour of aldehyde passed over the same mixture at a lower temperature gives acetate of potash and free hydrogen, losing only one equivalent of hydrogen and acquiring one of oxygen, or the reaction is similar to what occurs with the next substance to be mentioned, to which aldehyde has considerable analogy.* Oil of bitter almonds distilled with dry hydrate of potash, gives hydrogen gas and benzoate of potash.

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* Originally observed by Desfosses; Journal de Pharmacie, t. 14, p. 280 (1828).

According to the temperature, ulmic, acetic and oxalic acids appear in other cases, or carbonic acid only. Thus tartaric acid fused with hydrate of potash gives the acetate and oxalate of potash. Acetate of potash distilled with a mixture of hydrates of potash and lime, gives carbonate of potash and light carburetted hydrogen gas, which on that account is also named the gas of the acetates. Formic acid, alcohol, and bodies in general consisting of carbon, oxygen and hydrogen, when distilled with anhydrous barytes, give the same gas. When substances containing nitrogen are boiled in a solution of caustic potash, or fused with the dry hydrate, ammonia is evolved, and acids containing no nitrogen remain in combination with the potash. Some bodies containing much nitrogen lose only, with dry hydrate of potash, a portion of their nitrogen in the form of ammonia; and the rest acquiring oxygen, assumes the form of cyanic acid, and is protected by the potash from farther decomposition.

When the acetate of any metallic oxide capable of retaining carbonic acid at a red heat, such as the acetate of soda, potash, barytes, &c., is distilled, a carbonate remains in the retort, while a combustible liquid, acetone C_3H_3O distils over. M. Fremy has shewn that sugar, starch and all those ternary compounds of carbon, hydrogen and oxygen, in which the two last are in the proportion to form water, are decomposed when heated in contact with lime in the same manner as acetic acid. They afford acetone, with water and carbonic acid. Benzoic acid distilled with three times its weight of hydrate of lime forms carbonate of lime, with a volatile liquid $C_{12}H_6$, the benzin of Mitscherlich and bicarburet of hydrogen of Faraday. The neutral benzoate of lime gives with other products the liquid benzone, $C_{13}H_5O$. Distilled from lime stearic, margaric and oleic acids lose the elements of carbonic acid, and form neutral volatile products, stearone, margarone and oleone. The names of such pyrogen bodies terminate in *one* as contain one atom of oxygen and are neutral. Margarone carried in its turn over lime at a red heat, loses its oxygen, in the form of carbonic acid, and paraffin is produced, which is a binary compound of carbon and hydrogen. Thus the alkali determines throughout the formation of a highly oxidised acid body, with which it unites and the other products are consequently partially or completely deoxidised.

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* Annales de Chimie et de Physique, tome 73, p. 113.

Dry distillation.—Many organic substances are volatile and may be distilled at a moderate heat without alteration, such as alcohol and most essential oils; but a larger number are fixed. The latter when submitted alone to distillation usually abandon carbon, and form new and more simple volatile products. Three periods are distinguished by Liebig in the dry distillation of the fixed organic acids, from the different compounds formed according to the temperature. In the first, organic acids of less atomic weight are produced, with carbonic acid, water and inflammable liquids soluble in water. The bibasic and tribasic organic acids, by losing the elements of water and carbonic acid, are converted into their volatile pyr-acids, which are less basic, generally monobasic; thus tartaric acid $C_8H_4O_{10}$ is converted into pyrotartaric acid $C_5H_3O_3$, by losing three atoms of carbonic acid C_3O_6 and one atom of water HO; but these pyr-acids can rarely be distilled again by themselves, without partial decomposition. In the second period of the distillation, bodies are obtained which result from the destruction of the preceding compounds; thus the oxygen of the acids, uniting with the carbon and hydrogen of the combustible bodies, gives rise to more simple bodies, such as carbonic oxide, carbonic acid and water; some charcoal is generally set at liberty, while another portion of it enters into combination with the excess of hydrogen, and produces liquid or solid volatile hydrocarbons. In the last period, nothing is obtained but charcoal and a gaseous mixture, principally composed of carbonic acid, carbonic oxide, olefiant gas and light carburetted hydrogen. Substances containing nitrogen, give ammonia in the first period, and cyanogen or hydrocyanic acid in the last.

The decomposition of citric acid by heat, has been more minutely investigated than any other, by M. Crasso, and is particularly interesting from the variety of products it affords, at different stages of the decomposition. After losing its water of crystallization, the citric acid, $C_{12}H_5O_{11}$, first undergoes a decomposition, of which the products are a new and fixed acid, aconitic acid, $C_4 H_2 O_4$, also found in nature being the acid of the *aconitum napellus*, together with one atom of acetone. $C_3 H_3 O$, four atoms of carbonic oxide $C_4 O_4$, and one atom of carbonic acid $C O_2$. By a continuance of the heat, the fixed aconitic acid itself is decomposed, three atoms of it $C_{12} H_6 O_{12}$, affording two atoms of a volatile pyr-acid, named itaconic acid $2 (C_5 H_3 O_4)$, and two atoms of carbonic acid $C_2 O_4$. The itaconic acid again is decomposed when heated to its point of ebullition, and gives a more volatile and stable acid, named citraconic acid $C_5H_3O_4$, which is consequently isomeric with the preceding acid. It is believed, however, by Crasso, that the last is the only monobasic acid in the series, and that the true formulæ of the hydrates of the three new acids produced by the decomposition of citric acid by heat, are, with that of the original acid itself:

Citric acid. . . .	$C_{12} H_5 O_{11} + 3HO$
Aconitic acid. . .	$C_{12} H_6 O_{12} + 3HO$
Itaconic acid. . .	$C_{10} H_6 O_8 + 2HO$
Citraconic acid. .	$C_5 H_3 O_4 + HO$[*]

By the united action of heat and bases, other transformations of acids have been effected. Thus malic acid is converted into fumaric and equisetic acids, and citric acid into aconitic and tartaric acids, when their compounds with oxide of antimony or potash are heated so long as water is disengaged.

ACTION OFOXYGEN—EREMACAUSIS.

Organic compounds when dry and in a state of purity are generally capable of resisting the action of the air or of free oxygen, at the usual temperature; but a considerable number are affected by that element; the various essential and fixed oils absorb oxygen in different degrees, the first becoming resins and the second acquiring the drying properties of varnishes; the essential oil of bitter almonds is gradually converted into benzoic acid, and the vapour of ether passes slowly into acetic acid, while white indigo and other colouring principles undergo remarkable changes from a rapid absorption of oxygen. The direct oxidation of alcohol and ether, which gives rise to acetic acid, is greatly favoured by the contact of spongy platinum. The highly oxygenised acids act with much more energy upon organic compounds and give rise to various products according to the quantity of oxygen communicated. Thus alcohol is converted by oxidating matters, into acetal, aldehyde, acetic acid, formic acid, oxalic acid, carbonic acid and water. In these reactions, the oxygen is frequently observed to affect the hydrogen exclusively, which is converted into water, while a quantity of oxygen exactly equivalent to the hydrogen thus withdrawn, enters into combination with the remaining elements, and appears to be substituted for the hydrogen. Thus by the action of four atoms of oxygen, upon one atom of alcohol C_4H_5O+HO, two atoms of hydrogen are withdrawn as water, while two atoms of oxygen are at the same time absorbed by the remaining elements of the alcohol, which becomes hydrated acetic acid $C_4H_3O_3+HO$. When anhydrous sugar $C_{12}H_9O_9$ is treated with hypermanganate of potash, the nine atoms of hydrogen which the former contains are replaced by nine atoms of oxygen, and six atoms of oxalic acid formed $6C_2O_3$.

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[*] Annales de Chimie et de Physique, 3me Série, tome 1, p. 311.

The presence of water greatly promotes the action of the oxygen of the atmosphere upon organic substances. The name *eremacausis* has been applied by Liebig to the slow combustion or oxidation of organic matters in air. Vegetable juices evaporated by a gentle heat in air allow a brown or brownish black substance to precipitate, known as *extractive matter*, and similar in properties from whatever juice it is formed. It is insoluble or very sparingly soluble in water, but dissolved with facility by alkalies. By the action of air upon solid animal or vegetable matters, a similar pulverulent brown substance is formed known as *humus*. According to an observation of De Saussure, the sawdust of oak wood converts oxygen into carbonic acid, without any change of the volume of the gas; but while dry sawdust lost three parts by weight of carbon in this way, it diminished in weight by fifteen parts altogether, shewing that twelve parts of water were at the same time separated from the wood. Hence the proportion of carbon in decaying wood increases with the progress of its decay; and it is concluded that the hydrogen only is oxidised at the expense of the oxygen of the air, while the carbonic acid is formed from the elements of the wood (Liebig). The composition of pure woody fibre or lignin being $C_{36}H_{22}O_{22}$, two different specimens of mouldered oak wood, (the humus from oak wood) were found to be $C_{35}H_{20}O_{20}$ and $C_{34}H_{18}O_{18}$, or for every two atoms of hydrogen oxidised by the air, one atom of carbonic acid (CO_2) has been formed at the same time from the elements of the wood and set free. When water is present and the access of air restrained, the decomposition of wood appears to proceed in a different manner; for while carbonic acid is generated as before, a certain quantity of water enters into chemical combination, white mouldering beech-wood being found to have a composition corresponding with the formula $C_{33}H_{25}O_{24}$. There is reason, however, to suppose the interference in such cases of mouldering, of a species of fermentation such as was observed when rags were placed in heaps and wetted in the preparation of a substance for the fabrication of paper, according to the old process in use before the application of chlorine. The rags became warm and disengaged a gas, while their weight diminished from 18 to 25 per cent. It is probable that in this, as well as other putrefactive processes, the oxygen of the water assists in the formation of carbonic acid.

Wood coal or brown coal, which retains the structure of the wood unchanged, appears to be produced by a similar process of decomposition. A specimen free from bituminous matter was found to have a composition expressed by the formula $C_{33}H_{21}O_{16}$; and may therefore have been produced from woody fibre by the separation of one equivalent of hydrogen and three equivalents of carbonic acid. In all varieties of wood coal, the proportion of oxygen in relation to the hydrogen is diminished, these elements existing in the original woody fibre in the same proportion as in water, indicating a disengagement of carbonic acid from their substance, which appears still to go on at great depths in all the strata of wood coal. The composition of the splint coal of Newcastle and cannel coal of Lancashire being $C_{24}H_{13}O$, according to the analyses of both Richardson and Regnault, mineral coal is obviously formed from woody fibre in a different manner from brown coal. The composition of both splint and cannel coal is obtained by the subtraction of 3 atoms of carburetted hydrogen, 3 atoms of water, and 9 atoms of carbonic acid from the formula of wood (Liebig):

		$C_{36}H_{22}O_{22}$=wood.
Three atoms of carburetted hydrogen.	C_3H_6	
Three atoms of water.	H_3O_3	
Nine atoms of carbonic acid. .	C_9O_{18}	$C_{12}H_9O_{21}$
Mineral coal.		$C_{24}H_{13}O$

Caking coal from Caresfield, near Newcastle, is $C_{20}H_9O$, or contains the elements of cannel coal, *minus* the constituents of olefiant gas C_4H_4 (Liebig). The inflammable gas of coal mines is principally light carburetted hydrogen, but it has been observed by Bischoff occasionally accompanied by notable quantities of olefiant gas. Such decompositions, however, are not due to eremacausis, and indeed take place in materials covered by such a mass of strata as must entirely exclude air, but are more analogous to the internal reactions observed in organic matters, and known as species of fermentation, in which the elements of a compound substance (such as sugar) divide themselves into two or more groups, without the incorporation of any extraneous element, except perhaps the constituents of water.

The absorption of oxygen by alcohol in its acetification is a true eremacausis, so also is the process of nitrification. Oxidation is promoted in many organic bodies by contact with an alkali; thus alcohol holding potash in solution soon becomes brown from oxidation, and a resinous matter appears with all the products of the decomposition of aldehyde. The oxidation of gallic acid, hematin and many other compounds is promoted by the same influence; many vegetable substances exhibit a rapid absorption of oxygen on the addition to them of ammonia, and form splendid violet or red coloured liquids, such as the colouring principles of the lichens. On the other hand, eremacausis seems to be entirely prevented when water is excluded, or when the substance is exposed to a temperature of 32°. The processes of fermentation and putrefaction, which are different from eremacausis, appear to be necessarily preceded by an absorption of oxygen. Thus the juice of grapes pressed under mercury and collected in a jar filled with that metal was observed by Gay-Lussac to keep without change, but on admitting a bubble of air to the liquid, the vinous fermentation immediately commenced. The perfect exclusion of air is also the basis of the valuable process for preserving animal and vegetable food, without the use of antiseptics, first introduced by Appert. The materials are usually placed in canisters with a quantity of fluid, which is kept in a state of ebullition for some time, and the openings hermetically closed with solder while the vessels are entirely filled with steam. Eremacausis is also prevented or much retarded by aromatic substances, empyreumatic substances and oil of turpentine, the vapours of which retard the oxidation of phosphorus and of phosphuretted hydrogen in a similar manner. It is also arrested by mineral acids and salts of mercury, which appear to act by combining with the organic matter; alcohol, a strong solution of sugar, common salt and many other saline substances are supposed to owe their antiseptic properties in a great measure to their affinity for water, which reduces animal or vegetable matters in contact with them to a state of dryness in which they are little liable to decomposition. Thus a piece of dry butcher-meat covered with dry salt is found after twenty-four hours swimming in brine, the salt attracting water from the meat, and leaving it not humid enough for chemical action.

ACTION OF CHLORINE, ITS SUBSTITUTION FOR HYDROGEN, CHEMICAL TYPES.

M. Gay-Lussac observed, several years ago, that bees' wax exposed to chlorine gas absorbed the latter, giving rise to a disengagement of hydrochloric acid, without any change of volume in the gas from the operation. The reason is that the wax loses a volume of hydrogen equal to the volume of chlorine which it absorbs, the constituents of hydrochloric acid gas being united, it is to be remembered, without any condensation of volume. M. Dumas afterwards repeated the experiment with oil of turpentine, and obtained a similar result; 4H in the latter body being replaced by 4Cl, or $C_{20}H_{16}$ becoming $C_{20}H_{12}Cl_4$. The action of chlorine on a great number of organic substances has since been observed by MM. Dumas, Laurent, Regnault, Malaguti and others, and found to be remarkably uniform. The investigation has led to the formation of a large number of new compounds, and to the propagation of certain theoretical views by M. Dumas, which have had an extraordinary influence on the recent progress of organic chemistry.

When light carburetted hydrogen gas C_2H_4, is allowed to mix gradually with three times its volume of chlorine, in strong sunshine, the whole 4 eq. of hydrogen are converted into hydrochloric acid, which is liberated, while the 2 eq. of carbon combine with 4 eq. of chlorine, and form a peculiar liquid chloride of carbon C_2Cl_4; so that the hydrogen of the former compound appears to be simply replaced by chlorine in the latter.* The removal of the whole hydrogen by chlorine takes place at once, in this hydrocarburet without the formation of any other intermediate product except a trace of chloroform, but in other cases, where there are several equivalents of hydrogen, the latter are often removed and replaced by chlorine one by one, and a series of bodies formed in which while the hydrogen diminishes, the chlorine increases in an equal proportion; such are the compounds produced by the action of chlorine on Dutch liquid already described (page 375), and the remarkable series produced by the repeated action of chlorine upon hydrochloric ether.† The two series referred to, exhibit a remarkable isomerism, the corresponding products having the same composition although distinguishable by their physical properties and by the effect of re-agents upon them. These chlorine compounds are all volatile liquids, with the exception of the solid perchloride of carbon which is common to both series.

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[*] Dumas, An. de Ch. et de Ph. t. 73, p. 94.

[†] Regnault, An. de Ch. et de Ph. t. 71, p. 353.

OLEFIANT GAS AND BODIES DERIVED FROM IT BY THE ACTION OF CHLORINE.

Olefiant gas	C_4H_3+H
First product, Dutch liquid . .	$C_4H_3Cl+HCl$
Second product	$C_4H_2Cl_2+HCl$
Third product	$C_4H\,Cl_3+HCl$
Last product, perchloride of carbon .	C_4Cl_6

HYDROCHLORIC ETHER (CHLORIDE OF ETHYL) AND BODIES DERIVED FROM IT BY THE ACTION OF CHLORINE.

Hydrochloric ether	C_4H_5Cl
Monochlorinated ditto	$C_4H_4Cl_2$
Bichlorinated ditto	$C_4H_3Cl_3$
Trichlorinated ditto	$C_4H_2Cl_4$
Quadrichlorinated ditto	$C_4H\,Cl_5$
Perchloride of carbon	C_4Cl_6

It appears from the second table that hydrochloric ether is affected at once by two atoms of chlorine, one of which seizes an atom of hydrogen and removes it in the form of hydrochloric acid, while the second atom of chlorine enters into the compound remaining, which Regnault distinguishes as monochlorinated hydrochloric ether, the name having reference to the mode of derivation of the compound and not its composition.* The latter body when exposed to chlorine is likewise affected by two atoms, one of which seizes and withdraws an atom of hydrogen, while the other unites with the remaining elements, forming bichlorinated hydrochloric ether. The trichlorinated and quadrichlorinated compounds, and the perchloride of carbon, which follow, have the same mode of formation; and as one atom of chlorine is communicated for each atom of hydrogen withdrawn, the entire number of constituent atoms remains the same, or ten, throughout the series, and the last member differs only from the first, in having 5 atoms of chlorine instead of 5 of hydrogen. To exhibit the complimentary function of the chlorine and hydrogen in these bodies, their formulæ may be written thus:

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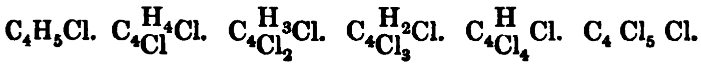
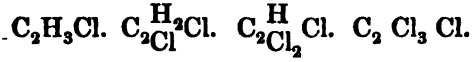
* "Chlorinated" appears to be a preferable term to *chloruretted*, to apply to such a compound, as the last is already used in a different sense.



$$C_4H_5Cl.\ \ C_4\genfrac{}{}{0pt}{}{H_4}{Cl}Cl.\ \ C_4\genfrac{}{}{0pt}{}{H_3}{Cl_2}Cl.\ \ C_4\genfrac{}{}{0pt}{}{H_2}{Cl_3}Cl.\ \ C_4\genfrac{}{}{0pt}{}{H}{Cl_4}Cl.\ \ C_4\,Cl_5\,Cl.$$

Chloromethylic ether or chloride of methyl C_2H_3Cl, a body having the same relation to wood-spirit that hydrochloric ether has to alcohol, gives rise to an analogous series of chlorinated compounds when a stream of chlorine is passed through it, the product being treated in its turn with the gas, and the same process repeated with the new product; when the hydrogen is then entirely withdrawn, and a chloride of carbon remains, the same that is derived from light carburetted hydrogen (Regnault). The bodies of this series are:—



$$C_2H_3Cl.\ \ C_2\genfrac{}{}{0pt}{}{H_2}{Cl}Cl.\ \ C_2\genfrac{}{}{0pt}{}{H}{Cl_2}Cl.\ \ C_2\,Cl_3\,Cl.$$

All these chlorinated compounds possess the neutral character of the bodies from which they are derived. Malaguti has also observed that ether (oxide of ethyl) may lose two equivalents of hydrogen and gain two of chlorine, C_4H_5O becoming $C_4H_3Cl_2O$, without any of its essential properties undergoing alteration; for its power of combination remains the same, and chlorinated ether is still ether. Oxalic ether or the oxalate of oxide of ethyl, may have its whole five atoms of hydrogen replaced by five atoms of chlorine, and chlorinated oxalic ether, or chloroxalic ether is formed; $C_4H_5O+C_2O_3$ becomes $C_4Cl_5O+C_2O_3$, or adopting empirical formulæ, $C_6H_5O_4$ becomes $C_6Cl_5O_4$. Now each of these ethers is the base of a class of salts, the oxalovinates and chloroxalovinates; each of them, also, is affected by dry ammoniacal gas, and by solution of ammonia in the same way, forming oxamethane or chloroxamethane with the first re-agent, and oxamide with the second:*

OXALIC ETHER, AND COMPOUNDS DERIVED FROM IT.

Oxalic ether . . .	$C_6H_5O_4$
Oxalovinic acid (hydrated)	$C_6H_5O_4+C_2O_3$, HO
Oxamethane . . .	$C_6H_5O_4+C_2O_2$, NH_2
Oxamide	C_2O_2, NH_2

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[*] Malaguti, Annales de Chimie, etc. t. 74, p. 299.

CHLOROXALIC ETHER, AND COMPOUNDS DERIVED FROM IT.

Chloroxalic ether . .	$C_6Cl_5O_4$
Chloroxalovinic acid (hydrated)	$C_6Cl_5O_4+C_2O_3$, HO
Chloroxamethane . .	$C_6Cl_5O_4+C_2O_2$, NH_2
Oxamide	C_2O_2, NH_2.

It rarely happens that the crystalline forms of corresponding hydrogen and chlorine compounds can be compared, for most frequently the two substances, or at least one of them, does not crystallize, and is altogether incapable of exact measurement. But M. de la Provostaye has succeeded in instituting a comparison between the crystalline forms of oxamethane and chloroxamethane, which he finds to be isomorphous, or rather different secondary forms derived from the same fundamental form.* This would establish the isomorphism of chlorine and hydrogen, but it is to be regretted that so important a conclusion should rest upon a single instance, and one also in which, as Mitscherlich remarks, the usual complete identity of form of isomorphous bodies is not observed.

By exposing pure acetic acid to the action of dry gaseous chlorine, under the direct influence of the solar rays, M. Dumas has replaced the whole hydrogen of that acid by chlorine, or converted acetic acid $C_4H_3O_3+HO$ into chloracetic acid $C_4Cl_3O_3+HO$, without altering the capacity of saturation of the acid, or its combining measure in the state of vapour.† Decomposed by alkalies, these two acids give likewise analogous products, acetic acid yielding carbonic acid C_2O_4 with light carburetted hydrogen, C_2H_4, and chloracetic acid yielding carbonic acid C_2O_4 with chloroform $C_2{}^{H}_{Cl_3}$; the body last mentioned being viewed as carburetted hydrogen in which three atoms of hydrogen are replaced by three of chlorine.

Many similar cases of the substitution of chlorine for hydrogen have been observed, but those already adduced are sufficient to illustrate the mode of replacement, and to prove that a compound may preserve its leading chemical characters, although its hydrogen be exchanged for chlorine. Chemists were not prepared for the admission of this equivalency of chlorine and hydrogen from anything observed in inorganic compounds. The two elements seemed, indeed, to be strongly contrasted, chlorine typifying the electro-negative or salt-radical class of elements, and hydrogen belonging, incontestably, to the electro-positive or basyle class with the metals, although not occupying a high place in that class. One equivalent of chlorine being also isomorphous with *two* equivalents of manganese, to which latter element hydrogen appeared to be related, as a member of the magnesian family, the isomorphous relation to be looked for was one of chlorine with two of hydrogen, and not with one of hydrogen as in oxamethane and chloroxamethane lately commented upon.

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* Philosophical Magazine, 3rd Series, vol. 18, p. 372.

† Annales de Chimie et de Physique, tome 73, p. 77.

But it is to be remembered that no body is absolutely chlorous (electro-negative), or zincous (electro-positive), but only relatively so to certain other bodies. Hence although zincous to chlorine, hydrogen is chlorous to carbon, or *hydrogen is the chlorous constituent of the organic compounds in question.* Even among inorganic compounds, we have instances of hydrogen discharging the same function, as in the class of phosphuretted hydrogen and arseniettted hydrogen, where 3 atoms of hydrogen are chlorous, and may be replaced by oxygen, chlorine, etc. (In ammonia, on the contrary, nitrogen appears to be the negative, and hydrogen the positive constituent.) In this way that universal dualism in the constitution of a compound, or distribution of its elements into two opposed classes, conducing to binary combination, which has never ceased to be a recognised doctrine of chemical science, in some form or other, with reference to inorganic compounds, is extended also to organic compounds. Such a doctrine which might always have been maintained on abstract grounds appears now to be inevitable from the observed substitutions of chlorine for hydrogen. Hydrogen then being viewed as a chlorous element in such compounds as carburetted hydrogen and olefiant gas, while carbon is the basyle or zincous element, the former element may therefore be replaced by other bodies higher than itself in the scale of salt-radicals, such as chlorine, without any essential derangement of the constitution of the original compound. The equivalent substitution of chlorine for hydrogen is thus admitted in its full extent. This substitution appears to confirm and extend what is generally understood at the electro-chemical distribution of elements, on which our ideas of binary combination are founded, and not to be opposed to or incompatible with such views.

The isomorphism of chlorine and hydrogen, equivalent for equivalent, if confirmed, will cause the removal of the latter element from the magnesian class, but establishes a relation between hydrogen and silver, and therefore places the former on the verge of the potassium group. Hydrogen certainly possesses many relations to mercury, if not absolutely isomorphous with that metal (page 656).

By a *chemical type* M. Dumas understands a certain number of elements combined together, every one of which, whatever be its nature, may be replaced by another, and indeed every one in its turn, so that not a trace of the original compound may remain. The arrangement of the elements in regard to each other remains always the same, and that is the character of the type. Thus all the chlorinated compounds derived from hydrochloric ether, including perchloride of carbon, contain ten atoms, which are supposed to have the same arrangement as in hydrochloric ether itself. Aldehyde produced by the partial oxidation of alcohol, and chloral by the action of chlorine upon alcohol, contain the same number of atoms and belong to one type:

$$\text{Aldehyde, } C_4H_3O + HO, \text{ or } C_4H_4O_2.$$

$$\text{Chloral, } C_4Cl_3O + HO, \text{ or } C_4\genfrac{}{}{0pt}{}{Cl_3}{H}O_2.$$

When on the other hand, an atom is withdrawn from a compound without being replaced by another, the atoms which remain cannot retain their original position, and a new type must result. It is supposed by Dumas, that chlorine may replace carbon, nitrogen and other elements besides hydrogen, and any one element, indeed any other, without destruction of the primitive type. Such substitutions however, have not been effected, and on the view of substitution taken above are not to be expected, for carbon at least must always be considered as the basyle or electro-positive constituent of organic compounds, and never like oxygen, nitrogen and hydrogen, as chlorous or electro-negative. Even where chlorine replaces hydrogen, the type is not uniformly preserved, for we find occasionally the same body derived by substitution from two different types, as perchloride of carbon from both Dutch liquid and hydrochloric ether.

The reference of bodies to a common type has often an advantage over their classification under a common radical or according to any theory of constitution, as it involves less that is speculative. The former asserts only that the bodies contain the same number of atoms and have a common constitution, but says nothing as to what that constitution is. Hence a type may be denoted by an empyrical formula of the simplest kind expressing nothing but the elements and their number, in which changes by substitution can be distinctly exhibited. It is useful, in the present uncertain state of our knowledge respecting the constitution of organic compounds, to have such a mode of expressing compounds and exhibiting their relations in composition, but it does not supersede rational theories of constitution.

TRANSFORMATIONS OF ORGANIC SUBSTANCES.

ACTION OF FERMENTS.

Complex organic substances frequently divide themselves into two or more compounds of a simpler constitution, without the intervention of any intelligible chemical agency. The presence of a second organic substance, however, is an essential condition of such transformations, although the latter substance does not contribute to the change by imparting any new element to the decomposing body, nor by abstracting any element from it. The resolution of sugar into carbonic acid and alcohol in fermentation, by the contact of yeast, is a familiar example of such a change (page 760). Decomposition of this kind has been distinguished as *catalysis*, and the second body which determines the changes in the first, by an action of presence, termed the *catalytic agent* (page 195). The recent study of such decompositions has revealed the circumstance that the activity of the catalytic agent is connected with its being itself in a state of decomposition at the time. The yeast is only active when, by access of air, it has become subject to oxidation, and the decomposition of the sugar is looked upon by M. Liebig as a reflex action of the decomposition of the yeast. The views of that eminent philosopher on the action of yeast and other ferments will be best explained in his own words.

"This action may be expressed by the following law, long since proposed by Laplace and Berthollet, although its truth with respect to chemical phenomena has only lately been proved. 'A molecule set in motion by any power can impart its own motion to another molecule with which it may be in contact.'"

This is a law of dynamics, the operation of which is manifest in all cases, in which the resistance (force, affinity, or cohesion,) opposed to the motion is not sufficient to overcome it.

We have seen that ferment or yeast is a body in the state of decomposition, the atoms of which, consequently, are in a state of motion or transposition. Yeast placed in contact with sugar, communicates to the elements of that compound the same state, in consequence of which, the constituents of the sugar arrange themselves into new and simpler forms, namely, into alcohol and carbonic acid. In these new compounds the elements are united together by stronger affinities than they were in the sugar, and therefore under the conditions in which they were produced further decomposition is arrested.

We know, also, that the elements of sugar assume totally different arrangements, when the substances which excite their transposition are in a different state of decomposition from the yeast just mentioned. Thus, when sugar is acted on by rennet or putrefying vegetable juices, it is not converted into alcohol and carbonic acid, but into lactic acid, mannite, and gum.

Again, it has been shown, that yeast added to a solution of pure sugar gradually disappears, but that when added to vegetable juices which contain gluten as well as sugar, it is reproduced by the decomposition of the former substance.

The yeast with which these liquids are made to ferment, has itself been originally produced from gluten.

The conversion of gluten into yeast in these vegetable juices is dependent on the decomposition (fermentation) of sugar; for, when the sugar has completely disappeared, any gluten which may still remain in the liquid, does not suffer change from contact with the newly-deposited yeast, but retains all the characters of gluten.

Yeast is a product of the decomposition of gluten; but it passes into a second stage of decomposition when in contact with water. On account of its being in this state of further change, yeast excites fermentation in a fresh solution of sugar, and if this second saccharine fluid should contain gluten, (should it be *wort*, for example,) yeast is again generated in consequence of the transposition of the elements of the sugar exciting a similar change in this gluten.

After this explanation, the idea that yeast reproduces itself as seeds reproduce seeds, cannot for a moment be entertained".*

To these may be added the results of the very recent inquiries of MM. Boutron and Fremy on the phenomena of the fermentation of malt. These chemists find that the same azotised matter in the grain, which acts as the ferment, passes through a succession of changes, and can excite different kinds of fermentation at different stages in the progress of its decomposition; that it is not one but a series of ferments. It is as diastase that it first appears, or this is the first condition of the ferment in the infusion of malt, as is proved by the action which it exerts upon starch, the latter being converted into sugar. From the acidity of the liquor which is afterwards observed, it is evident that the azotised matter next takes the character of the lactic ferment (page 808), and converts the sugar, to a certain extent, into lactic acid. A period then arrives at which the liquid, still transparent, becómes turbid, and the resulting precipitate is the matter which can produce the alcoholic fermentation; and it is only at this epoch that alcohol is formed and carbonic acid disengaged. That it is the insoluble precipitate to which the alcoholic fermentation should be ascribed, is proved by filtering the liquid to separate the ferment, when the alcoholic fermentation is immediately arrested.†

The action of yeast and all other ferments is destroyed by the temperature at which water boils, by alcohol, by acids, salts of mercury, sulphurous acid, chlorine, iodine, bromine, by aromatic substances, volatile oils, and particularly empyreumatic oils, smoke and a decoction of coffee, these bodies in some cases combining with the ferments or otherwise effecting their decomposition.

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* Liebig's Organic Chemistry in its applications to Agriculture and Physiology, edited by Dr. Lyon Playfair.

† Ann. de Chim. &c. 3 serie, t. 2, p. 269.

The following are additional instances of fermentation. The smell and taste which distinguish wine from all other fermented liquids depend upon *œnanthic ether*, which contains a peculiar acid; and those of spirits from corn or potatoes upon a peculiar oil, the *oil of potatoes*. Both of these substances are produced in fermentation, the former probably from the tartaric acid of the wine, the latter by a simultaneous decomposition of the cellular tissue of the grain or potato. The oil of potatoes has all the characters of an alcohol (page 813). The production of this oil is completely prevented in the fermentation of beer, by the presence of an aromatic substance, the volatile oil of hops. In the fermentation of the *Herba centaurium minorius*, a plant which possesses no smell, a true ethereal oil is formed, of a penetrating agreeable odour. The leaves of tobacco, when fresh, have little or no smell, and when distilled, yield a white, fatty, crystallizable substance (nicotianine), which contains no nitrogen and is quite destitute of smell. But when the same plant, after being dried, is moistened with water, tied together in small bundles, and placed in heaps, a peculiar process of decomposition takes place. Fermentation commences, and is accompanied by the absorption of oxygen; the leaves now become warm and emit the characteristic smell of prepared tobacco and snuff. When the fermentation is carefully promoted, and too high a heat avoided, this smell increases and becomes more delicate; and after the fermentation is completed, an oily azotised volatile matter, called *nicotine*, is found in the leaves. This substance which possesses all the properties of a base, was not present before the fermentation. The different kinds of tobacco are distinguished from one another, like wines, by having very different odoriferous substances, which are generated along with the nicotine (Liebig).

M. Liebig also ascribes the morbific action of matters of contagion and miasms, to their operation as ferments. He applies the law already quoted to organic substances forming part of the animal organism. "We know that all the constituents of these substances are formed from the blood, and that the blood by its nature and constitution is one of the most complex of all existing matters.

Nature has adapted the blood for the reproduction of every individual part of the organism; its principal character consists in its component parts being subordinate to every attraction. These are in a perpetual state of change or transformation, which is effected in the most various ways through the influence of the different organs.

The individual organs, such as the stomach, cause all the organic substances conveyed to them which are capable of transformation to assume new forms. The stomach compels the elements of these substances to unite into a compound fitted for the formation of the blood. But the blood possesses no power of causing transformations; on the contrary, its principal character consists in its readily suffering transformations; and no other matter can be compared in this respect with it.

Now it is a well-known fact, that when blood, cerebral substance, gall, pus, and other substances in a state of putrefaction, are laid upon fresh wounds; vomiting, debility, and at length death, are occasioned. It is also well known that bodies in anatomical rooms frequently pass into a state of decomposition which is capable of imparting itself to the living body, the smallest cut with a knife which has been used in their dissection producing in these cases dangerous consequences.

The poison of bad sausages belongs to this class of noxious substances. Several hundred cases are known in which death has occurred from the use of this kind of food. In Wirtemberg especially, these cases are very frequent, for there the sausages are prepared from very various materials. Blood, liver, bacon, brains, milk, meal and bread, are mixed together with salt and spices; the mixture is then put into bladders or intestines, and after being boiled is smoked. When these sausages are well prepared, they may be preserved for months, and furnish a nourishing savoury food; but when the spices and salt are deficient, and particularly when they are smoked too late or not sufficiently, they undergo a peculiar kind of putrefaction which begins at the centre of the sausage. Without any appreciable escape of gas taking place, they become paler in colour, and more soft and greasy in those parts which have undergone putrefaction, and they are found to contain free lactic acid or lactate of ammonia; products which are universally formed during the putrefaction of animal and vegetable matters.

The death which is the consequence of poisoning by putrefied sausages succeeds very lingering and remarkable symptoms. There is a gradual wasting of muscular fibre, and of all the constituents of the body similarly composed.

Sausages, in the state here described, exercise an action upon the organism, in consequence of the stomach and other parts with which they come in contact not having the power to arrest their decomposition; and entering the blood in some way or other, while still possessing their whole power, they impart their peculiar action to the constituents of that fluid.

MOLECULAR THEORY OF ORGANIC COMPOUNDS.

It is observed by Liebig that in all organic compounds it is necessary to consider two kinds of attraction, that of the contained radicals, and that of the ultimate elements themselves for each other; which last attraction is not superseded by the former. To these elemental attractions we are to look for an explanation of the phenomena of substitution.

Any theory of combination would be incomplete which did not provide in the constitution assigned to both elementary and compound bodies, for that propagation of chemical action to a distance which is witnessed in the voltaic circle. The consideration of that action has already forced upon us the conclusion that even a free element such as a metal, in the state in which we operate with it, has a complex molecular structure, its atoms being grouped, so as to represent binary compounds. Hence in combining two different elements, we have really to undo a previous but weaker combination in both cases, before the dissimilar elements unite; and consequently, even where combination appeared most direct, we have the compound really formed by a mutual double decomposition, or by the substitution of one element for another in pre-existing frames of compounds. The universal susceptibility of compounds of all kinds to decomposition under electrical action of high intensity, appears also to argue a greater simplicity and sameness of constitution of chemical compounds than is generally recognised.

We are repelled by the idea of atoms of the same kind having the relation to each other of combination, for diversity of nature appears to be the reason why bodies combine. The intensity of the combination certainly increases with the diversity, but this does not prove that such diversity is an essential condition of combination. Combination, indeed, appears to be the natural condition of matter, the source of its cohesion and aggregation, which it retains by inertia, and decomposition to require the application of a force, such as the communication of heat to atoms which supplies them with the repulsive power required to overcome their combination.

The fundamental elemental combination of every compound is assumed to be binary, one element being chlorous (negative), and the other zincous or basic (positive); or one set of the elements being chlorous, and another set basic. This difference in the character of the elements of a compound may be expressed by writing its formula in two lines, placing the basic or positive elements in the lower, and the chlorous or salt-radical elements in the upper line:

Water $\frac{O}{H}$, carbonic acid $\frac{O_2}{C}$, hydrate of potash $\frac{O.O}{K.H}$, carbonate of potash $\frac{O_2.O}{C\,.K}$, olefiant gas $\frac{H_4}{C_4}$, or $\frac{H_2.H_2}{C_2.C_2}$; ether $\frac{H_5O}{C_4}$, alcohol $\frac{H_5O.O}{C_4.\ H.}$

Most of these formulæ are meant only to express that certain elements collectively are chlorous and certain others collectively basic. In ether, for instance, 4 atoms (C_4) are basic, against 6 atoms (H_5O) chlorous; but it is to be supposed that many compounds admit of a division into more simple binary compounds, olefiant gas $\frac{H_4}{C_4}$ into two binary compounds $2C_2H_2$, expressed thus, $\frac{H_2.H_2}{C_2.C_2}$; or even four binary compounds 4CH, expressed thus, $\frac{H.H.H.H}{C.C.C.C}$. No particular binary arrangement of this kind, however, is at present insisted upon, unless in a few cases. All that is assumed is:

1. That the basic or positive element or elements are in immediate combination with the chlorous element or elements placed above them in the formulæ.

2. That these binary compounds again are *associated together* so as to form the compound molecule, from an attraction of all the basic elements for each other, and of all the chlorous elements for each other, of such a nature as retains together the 3 atoms of the same kind which form a single equivalent of nitrogen or phosphorus, the 3 atoms of cyanogen in cyanuric acid, the various multiples of C_2H_2 grouped together in the molecule of olefiant gas and hydrocarbons isomeric with it, or the multiples of C_5H_4 in the molecule of oil of turpentine and a large class of essential oils. *A complex organic molecules is thus represented as an association of two or more binary compounds, comparatively simple in constitution, often isolable substances and possessed of considerable stability.*

In the superior or chlorous portion of the formulæ of organic compounds we may generally expect to find chlorine, oxygen, nitrogen, hydrogen; and in the inferior or basic portion, carbon, or carbon and hydrogen. The former elements appear to be chlorous in the order in which they are enumerated:

Chlorine
Oxygen
Sulphur
Nitrogen
Hydrogen.

We find in substitutions, those in the lower part of the table replaced by those above them, hydrogen at the bottom of the table eminently so by chlorine at the top, and hydrogen also by oxygen. Nitrogen less frequently interferes, but it appears in certain cases more chlorous than oxygen and to replace that element; only, however, in certain double decompositions as an element of ammonia, which are not sufficient to determine its place, as oxygen might be placed above chlorine from similar indications, as the conversion of chloroform $FoCl_3$ into formic acid FoO_3 by potash.

Compounds of the same type.—These are bodies which have the same number of elementary atoms, and the same numbers of them chlorous and zincous. As:

Of olefiant gas type: olefiant gas $\frac{H_4}{C_4}$; chloride of carbon $\frac{Cl_4}{C_4}$.

Of ether type: ether $\frac{H_5O}{C_4}$; chloride of ethyl $\frac{H_5Cl}{C_4}$; chlorinated ethyl $\frac{H_4Cl_2}{C_4}$, &c.

Of alcohol type: alcohol $\frac{H_5O.O}{C_4.\ H}$; acetic acid $\frac{H_3O_3.O}{C_4.\ H}$; chloracetic acid $\frac{Cl_3O_3.O}{C_4.\ H}$.

Of aldehyde type: aldehyde $\frac{H_3O.O}{C_4.\ H}$; chloral $\frac{Cl_3O.O}{C_4.\ H}$.

Ammonia.—The molecular formula of ammonia appears to be $\frac{N}{H_3}$, and not $\frac{H_3}{N}$. The hydrogen of ammonia being basic, according to the first formula, should not be replaced by chlorine, and certainly chlorinated salts of ammonia, analogous to the chlorinated compound ethers, have not been observed. Our knowledge of the composition of the explosive chloride of nitrogen is not sufficiently certain to decide the question. It will be remembered that N in the formula above is equivalent to O_3 or H_3. Wöhler's white precipitate of mercury $HgCl + NH_3$ (page 656), and ordinary white precipitate, $HgCl + HgNH_2$, are assimilated, being expressed respectively by: $\frac{Cl\ .N}{Hg.H_3}$, and $\frac{Cl.\ \ N}{Hg.\ H_2Hg}$.

The black compound, produced by solution of ammonia upon calomel, is expressed by $\frac{Cl.\ \ \ N}{Hg_2.\ H_2Hg_2}$, or possibly by $\frac{ClHg.\ \ N}{Hg_2.\ H_2Hg}$. Thus amidogen is not necessarily present in the supposed metallic amides; but appears to be more necessary to the constitution of oxamide and urea, particularly the last. Of oxalate of ammonia, and oxamide, the molecular formulæ are: $\frac{O_3.O.N}{C_2.H.H_3}$ and $\frac{O_2N.}{C_2.H_2}$.

Cyanogen and cyanides.—The formula for cyanogen is

$\frac{N}{C_2}$; for hydrocyanic acid $\frac{NH}{C_2}$, and not $\frac{N}{C_2H}$. That the hydrogen of hydrocyanic acid is chlorous and not basic, appears in its being replaced by chlorine, with formation of hydrochloric acid and the chloride of cyanogen, $\frac{NCl}{C_2}$. Hence, also, the little action of potash and strong bases upon hydrocyanic acid (page 989), its hydrogen, unlike that of ordinary hydrogen acids, being chlorous, while the same hydrogen is readily replaced by the more chlorous metals, such as mercury, the cyanide of mercury being $\frac{NHg}{C_2}$. The latter salt is not decomposed by strong acids, as it would be if its constitution resembled that of cyanide of potassium $\frac{N}{C_2K}$. But cyanide of mercury is readily decomposed by sulphur and sulphuretted hydrogen, and by hydrochloric acid, sulphur and chlorine assuming the mercury and forming sulphuret and chloride of mercury respectively, while hydrogen is left in the place of the abstracted mercury, and hydrocyanic acid $\frac{NH}{C_2}$ reproduced.

The two atoms of cyanide of hydrogen, which exist in *ferrocyanic acid*, $FeCy+2HCy$, have, on the contrary, the constitution of an ordinary hydrogen-acid, the hydrogen being strongly basic and easily replaced by the basic metals, potassium &c. while the iron is not. It thus contains $\frac{N_2}{C_4H_2}$. But the iron of the associated cyanide of iron not being precipitated by potash (replaceable by potassium), must be chlorous; and this metallic cyanide, therefore, resembles ordinary hydrocyanic acid in constitution, or is $\frac{NFe}{C_2}$.

Ferrocyanic acid . . . . $\frac{NFe}{C_2} \cdot \frac{N_2}{C_4H_2}$

Ferrocyanide of potassium. $\frac{NFe}{C_2} \cdot \frac{N_2}{C_4K_2}$

The molecular formulæ for *ferricyanic acid* $(H_3+Fe_2Cy_6)$, and for *ferricyanide of potassium* $(K_3+Fe_2Cy_6)$, deducible from the same principles, are :

Ferricyanic acid . . . . . $\dfrac{N_3Fe_2\ .\ N_3}{C_6\ .\ C_6H_3}$

Ferricyanide of potassium . $\dfrac{N_3Fe_2\ .\ N_3}{C_6\ .\ C_6K_3}$

Assigning to *sulphocyanogen*, C_2NS_2, the molecular formula $\frac{NS_2}{C_2}$, its compounds will be:

Hydrosulphocyanic acid . . $\dfrac{N\ S_2}{C_2H}$

Sulphocyanide of potassium . $\dfrac{N\ S_2}{C_2K}$

Hydrated *cyanic acid* and cyanate of potash will be represented by formulæ which assimilate them to the preceding compounds:

Hydrated cyanic acid . . $\dfrac{NO_2}{C_2H}$,

Cyanate of potash . . . $\dfrac{NO_2}{C_2K}$.

The two isomeric bodies *cyanate of ammonia* and *urea* (page 392) have different molecular formulæ:

Cyanate of ammonia . $\dfrac{N\ O_2.\ N}{C_2H\ .\ H_3}$

Urea . . . . $\dfrac{N\ .O_2.\ N}{C_2.H_2.H_2}$

In the last formula urea is represented as containing 1 atom of cyanogen, 2 atoms of water and 1 atom of amidogen. According to the more common opinion, it contains 2 atoms of carbonic oxide and 2 atoms of amidogen, a view which may be expressed by making a slight change in the upper line of the preceding formula:

Urea . . . . . . $\dfrac{O_2.N\ .N}{C_2.H_2.H_2}$.

But the existence of cyanogen in urea being probable, the first formula is preferable. Urea may then be compared with *allantoin*, which contains 2 atoms of cyanogen and 3 atoms of water:

Allantoin . . . $\frac{N_2.O_3}{C_4.H_3}$, or $\frac{N\ .O_3.N}{C_2.H_3.C_2}$.

Doubling the atom of allantoin, that substance and its compound with oxide of silver will be:

$$\frac{N_4.O_6}{C_8.H_6} \text{ and } \frac{N_4.\ O_6}{C_8.H_5Ag}$$

From the different action of potash upon the isomeric bodies, *Dutch liquid* and *protochlorinated chloride of ethyl*, there can be little doubt but their molecular formulæ are really different: Dutch liquid $\frac{H_3Cl.Cl}{C_4\ .\ H}$; protochlorinated chloride of ethyl $\frac{H_4Cl_2}{C_4}$; and while the other chlorinated compounds of chloride of ethyl are $\frac{H_3Cl_3}{C_4}$ and $\frac{H_2Cl_4}{C_4}$, those of olefiant gas, isomeric with the preceding, are, as appears by the action of an alkali, $\frac{H_2Cl_2.Cl}{C_4\ .\ H}$, and $\frac{HCl_3.Cl}{C_4.\ H}$. For from Dutch liquid and the two last mentioned compounds, potash withdraws HCl, and liberates three compounds of the same type: $\frac{H_3Cl}{C_4}$, $\frac{H_2Cl_2}{C_4}$ and $\frac{HCl_3}{C_4}$.

The elements which are chlorous together or basic together in a compound, certainly exert an influence upon each other, although they are not to be supposed to be combined, as those of different name are, with each other. For we find a tendency among them to arrange themselves in pairs. Thus the chlorinated compound of oxide of ethyl, most readily formed, is that of which the empyrical formula is $C_4H_3Cl_2O$, and the molecular formula $\frac{H_3Cl_2O}{C_4}$, or rather $\frac{H_2Cl_2HO}{C_4}$, of which the three atoms of hydrogen are associated with three still more chlorous atoms namely two of chlorine and one of oxygen. There can be no doubt that these three remaining atoms of hydrogen are thus in some degree defended from the farther action of chlorine, and less easily removed than the other two.

The molecular formula of oil of bitter almonds, or hydruret of benzoyl appears to be $\frac{H_6O_2}{C_{14}}$; of hydrated benzoic acid $\frac{H_5O_3.O}{C_{14}.\ H}$.

Of the *oil of spiræa* or *salicylous* acid, which is isomeric with the last, $\frac{H_5O_4}{C_{14}H}$; of chlorosalicylous acid, $\frac{H_4O_4Cl}{C_{14}H}$; and of hydrated salicylic acid, $\frac{H_5O_6}{C_{14}H}$, or $\frac{H_5O_5.O}{C_{14}.\ H}$.

The peculiarity of oil of spiræa, or salicylous acid, is that its single basic atom of hydrogen is removeable by itself, like that of a hydrogen acid, in the formation of salts, while of hydrated benzoic acid, both H and O are removed in the formation of salts. This difference is expressed in their molecular formulæ.

The hydrated and bibasic *bromobenzoic acid* is an association of two acids, one of which differs from the other in having an atom of hydrogen replaced by bromine; namely $HO+C_{14}H_5O_4$ and $HO+C_{14}H_4BrO_4$. Of these two the molecular formulæ may be, of the first, $\frac{H_5O_4.O}{C_{14}\ .\ H}$ and of the second $\frac{H_4O_4Br.O}{C_{14}.\ H}$.

Of *benzamide*, Bz+Ad, or $C_{14}H_5O_2+NH_2$, the molecular formula may be $\frac{H_5N.O_2}{C_{14}H_2}$, in which N replaces 3O of hydrated benzoic acid.

Of *hydrobenzamide*, $C_{14}H_6N_{\frac{2}{3}}$, produced by the action of ammonia on the hydruret of benzoyl, the molecular formula is $\frac{H_6N_{\frac{2}{3}}}{C_{14}}$; or that of the oil, with 2O replaced by $N_{\frac{2}{3}}$.

Of *salicylimide*, $HO+C_{14}H_5ON_{\frac{2}{3}}$, produced by the action of ammonia on salicylous acid, $\frac{H_5O_2N_{\frac{2}{3}}}{C_{14}H}$, or $\frac{H_5N_{\frac{2}{3}}O.O}{C_{14}\ .\ H}$; that is, salicylous acid with 2O replaced by $N_{\frac{2}{3}}$

Of *chlorosalicylimide*, $C_{14}H_3Cl_3O_2N_{\frac{2}{3}}$, $\frac{H_2Cl_3N_{\frac{2}{3}}O_2}{C_{14}H}$, or $\frac{Cl_3H_2O_2N_{\frac{2}{3}}}{C_{14}H}$; three atoms of the chlorous hydrogen of salicylimide being replaced by chlorine.

Formation of acids.—The formula of benzole or benzin, is $\frac{H}{C_{12}}$; of the neutral body, sulphobenzide, $\frac{H_5SO_2}{C_{12}}$, or $\frac{H_5O_2.}{C_{12}S}$ To the last hydrated sulphuric acid is attached, in *sulphobenzic acid* $=\frac{H_5O_2.O_3.O}{C_{12}S.S.\ H}$, or $\frac{H_5SO_2.O_3.O}{C_{12}\ .S\ .H}$.

Sulphurous acid, SO_2, is a body like sulphobenzide; in hyposulphuric acid it has hydrate of sulphuric acid attached to it. Sulphurous acid, $\frac{O_2}{S}$; hydrated hyposulphuric acid, $\frac{O_2.O_3.O}{S.\ S.H}$

The neutral substance, *benzile*, $C_{14}H_5O_2$, or $C_{28}H_{10}O_4$, becomes benzilate of potash, by fixing the elements of hydrate of potash; thus benzile, $\frac{H_{10}O_4}{C_{28}}$; benzilate of potash, $\frac{{}_{10}O_4.\ \ .O}{C_{28}.\ H.K}$ When the potash is withdrawn from the latter by a stronger acid, hydrated benzilic acid is formed, $\frac{H_{10}O_4.O.O}{C_{28}.\ H.H}$. When neutralised with bases, this hydrate loses an atom of water and acquires an atom of metallic oxide in its place.

Chlorisatin, a neutral substance, when dissolved in caustic potash is converted into chlorisatinate of potash, in a similar manner: Chlorisatin, $\frac{H_4ClO_3N}{C_{32}}$; chlorisatinate of potash, $\frac{H_4ClO_3N.O.O}{C_{16}\ \ H.K}$. Decomposed by a strong acid, the latter salt gives hydrate of *chlorisatinic acid*, $\frac{H_4ClO_3N.O.O}{C_{16}\ .\ H.H}$

Concentrated acids decompose this hydrate, assuming its water, and reproduce the neutral chlorisatin. It is clear that the anhydrous acids generally, such as SO_3, PO_5, &c., belong to the class of sulphobenzide and chlorisatin, and owe their power of combining with bases to the association with them of an atom of water.

Hydrate of sulphuric acid, $\frac{O_3.O}{S.H}$; hydrates of phosphoric acid, $\frac{O_4.O}{P.\ H}$, $\frac{O_5.O_2}{P.H_2}$ and $\frac{O_5.O_3}{P.H_3}$.

We have other series of compounds of which the members only differ from each other, in containing different proportions of water or its elements attached to a common basis, as starch, gum and starch sugar; gum being starch plus 1 atom of water; and starch sugar, starch plus 2 atoms of water. It is at present impossible, however, to assign a probable molecular formula to the basis of the starch and many other series of compounds, from our ignorance of the function of the hydrogen in their constitution, where the hydrogen has not been replaced by another element more decidedly chlorous or basic in its character.

CHAPTER II.

SECTION I.

AMYLACEOUS AND SACCHARINE SUBSTANCES.

STARCH.

Syn. FECULA, AMYLIN; $C_{12}H_{10}O_{10}$; in combination with oxide of lead, $C_{12}H_9O_9+2PbO$, (Payen). Its composition, well dried in vacuo at 212°, is

12 atoms of carbon. . . .	917.22..	44.91
10 atoms of hydrogen. . .	125.00..	6.11
10 atoms of oxygen. . . .	1000.00..	48.98
	204.22..	100.00

Starch is separated from a variety of vegetable substances containing it, from the grains of the different cereals, many roots such as the potato, the stems of many monocotyledonous plants particularly the palms, and from several lichens. It is contained in the cavities of the vegetable cells, in the form of small white and brilliant grains, which are not crystalline, but have a rounded outline without any determinate form. It is so far an organised substance, that each grain has a species of envelope, which resists the action of cold water, while the inner portion is observed by the microscope to be composed of concentric layers of unequal thickness, as if the layers produced during the day exceeded in thickness those formed during the night. (Fritzsche). The grains of the starch of different plants differ in size, those of the potato being about $\frac{1}{300}$, of wheat $\frac{1}{500}$, of millet, $\frac{1}{10000}$th of an inch in diameter, according to observations of Raspail. But it is also known that the starch grains of the same plant differ in size at different stages of its development.

The purest starch is obtained from potatoes, which are reduced to a pulp and washed on a sieve. The grains of starch are separated and passed through; they may be washed repeatedly with cold water. Potatoes yield 15 to 17 per cent. of starch; wheaten flour consists essentially of starch and another vegetable principle gluten. When made into dough with a little cold water, inclosed in a linen bag, and gently pressed by the hand in water, so long as a milky juice exudes, these two substances are in a great measure separated, the gluten remaining in the bag, and the grains of starch being diffused through the water, from which they afterwards subside. On the large scale, wheaten meal coarsely ground is mixed with cold water in large vats, in which, with a certain addition of sour water from a former process, the liquid ferments for seven or eight days, and the starch subsides. The acetic acid formed in the fermentation dissolves the greater part of the gluten of the flour, and the bran is separated from the starch by a fine sieve. The starch is afterwards mixed with pure water in the vat and allowed to settle; the remaining gluten is deposited as a grey slimy matter above the starch, which is removed, and the starch washed again till pure. For the fermentation, the action of a weak solution of caustic alkali has lately been substituted, by which the gluten of flour is dissolved and the starch left. Mr. O. Jones employs a ley containing 200 grains of caustic soda in one gallon of water. A ley containing 400 grains of soda causes the starch to gelatinize; by that quantity of ley, one pound of excellent starch is obtained from flour of rice, allowed to digest in it in the cold for forty-eight hours.

Arrow root is the starch from the root of the marantha arundinacea. It is not accompanied by any odoriferous principle, and has therefore no smell when boiled with water, in which respect it resembles potato starch washed with alcohol. *Sago* is derived from the pith of true palms of the genus Sagus; *tapioca* or *cassava*, from an American plant, the iatropha manihot, of which the milky juice, itself poisonous, deposits when diffused through water a harmless starch. The peculiar appearance and solubility in cold water of sago and tapioca arise from the starch being exposed while humid to a temperature above 140°, so that it is dried in the gelatinous condition and not in the original grains.

Starch or fecula may be purified from adhering gluten by maceration in diluted acetic acid, or by means of a cold and dilute solution of alkali. The starch of commerce is perfectly white, and in small columns formed by the contraction of the humid mass of starch in drying, which are easily reduced to a fine powder. It emits a particular sound when pressed between the fingers, its density is 1.53. The other characters which fecula exhibits are complete insolubility in cold water and in alcohol, but resolving itself in boiling water into a mucilaginous liquid, which forms a jelly on cooling. This when suddenly dried upon linen imparts considerable stiffness to it. Dilute acids dissolve starch, and form a transparent and highly fluid liquid. When this solution is boiled for a long time, the starch is first converted into a body having the properties of gum, and afterwards into starch sugar. Nitric acid with the assistance of heat converts starch into oxalic and malic acids, without producing a trace of mucic acid. Starch is also soluble in alkalies; when brayed with a concentrated solution of hydrate of potash, it forms a transparent gelatinous compound soluble in alcohol and water, from which the starch is precipitated by acids. Starch is precipitated from solution by lime water and hydrate of barytes, and by sub-acetate of lead containing ammonia, forming insoluble compounds with lime, barytes and oxide of lead. A solution of starch is also coagulated by borax, which combines with and precipitates the starch, but not by boracic acid. Starch is precipitated by an infusion of gallnuts. It forms a blue insoluble compound with iodine.

Gelatinous starch or amidin.—In this state starch appears to retain a portion of its organisation or structure, upon which some of its properties depend, and which is the cause of the difference in properties of the varieties of starch, containing the same chemical principle. When grains of fecula are rubbed in a mortar with sand, their coating is broken and they form a greyish white powder, which when mixed with a little cold water immediately expands and forms a transparent jelly. If the uninjured grains be thrown into water above 140°, they imbibe water, swell and burst their envelopes, which have a certain degree of elasticity, and undergo the same change. But the gelatinous starch has imbibed water like a sponge, without being dissolved and when placed upon several folds of blotting paper imparts to the latter its moisture, and dries up into a mass resembling horn, which exhibits again the same phenomena, when after being reduced to powder it is treated with boiling water. A portion of the gelatinous starch, however, appears to be dissolved by a large quantity of cold water, about $\frac{1}{8}$th of the starch, when the 'bruised grains are diffused through 100 times their weight of cold water, and the whole of it when gelatinous starch is boiled with 40 or 50 parts of water; for the mucilaginous liquid passes through a double paper filter and no granules or solid matter in any other form can be perceived in the liquid by the microscope. The tegumentary portion of the starch, which amounts to three or four thousands of the whole, remains on the filter, but may also be dissolved by continued boiling. When the quantity of starch dissolved by hot water is considerable, much of the starch separates in a gelatinous state, on the cooling of the solution. The peculiar character of the solution of starch in water has been the object of much research by M. Payen, which lead to the observation that by the freezing of a solution of starch that substance separates from the water and contracts into a species of tissue, which is not dissolved again on the thawing of the ice. It is the opinion of the same chemist that the organisation of the starch is not altogether effaced or its cohesion destroyed, so long as it is gelatinous and possesses the property of being stained by iodine of a blue, or of different shades of violet to red, according to the degree of its division.*

Granules of starch of M. Jacquelain.—When starch is heated under pressure in a Papin's digester to 302° (150° cent.), with from five to fifteen times its weight of water for two hours, the whole is dissolved except the tegumentary matter, and the solution is so thin that it may be filtered at the boiling temperature. This solution when it cools deposits a considerable mass of pulverulent matter, white and opaque and entirely composed of a species of granules; first observed by M. Jacquelain. These granules when examined by a microscope having a power of 200 diameters, present themselves as circular or spherical bodies, transparent, and uniformly $\frac{1}{1500}$ of an inch ($\frac{2}{100}$ths of a millimetre) in diameter. When dried they have the whiteness of starch without its lustre. They are denser than water, and subside from that liquid almost as quickly as fecula. These granules are scarcely soluble at 32°, slightly so at 53.6°, but dissolve in a considerable proportion about 158°, and in still greater quantity at the temperature of ebullition. This increased solubility is the most remarkable chemical change which the starch has undergone, by its solution in water at a high temperature. Anhydrous alcohol precipitates completely a solution of the granules and the aqueous solution of iodine makes it blue and not purple. When a film of a concentrated solution of these granules is left under the microscope, it is seen to be in a state of agitation so long as the evaporation of the water continues and when the matter comes to be dried, the granules cease to be visible, attaching themselves to each other as if soldered together, and forming a transparent plate in which nothing can be perceived even with a magnifying power of 800 diameters. A solution of the granules, when frozen and afterwards melted, gives the granules in the form of fine filaments, which are very short, and have a silky lustre. M. Jacquelain finds these granules and fecula, both dried between 266° and 275°, to have the same composition, $C_{12}H_{10}O_{10}$. But he constantly obtained a small quantity of nitrogen from starch, about ½ per cent. from his granules and a somewhat larger proportion from fecula, which he conceives to be essential to that substance. The power which starch possesses to form these granules, must be considered as an organic property, and proves that it retains contractility, even when dissolved in water.* The original grains of fecula, which consist of concentric layers, are still more highly organised; starch indeed occupies an important place in organic chemistry, as a link between matters truly organised and those bodies of a less complex constitution, which still belong to the organic kingdom, but approach in their crystallization, volatility or chemical properties to mineral substances properly so called.

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* Annales de Chimie et de Physique, tome 65, p. 225.

A compound of amidin and oxide of lead was formed by M. Payen, by dissolving two parts of pure starch in 250 parts of water, with ebullition for twenty minutes and pouring the filtered solution into an excess of the ammoniacal solution of acetate of lead (page 594), collecting and washing the precipitate upon a filter, and drying it in vacuo at 356° (180° cent.) He terms it the bibasic amylate of lead, $C_{12}H_9O_9+2PbO$.

Starch combines with chlorine, bromine and iodine. The solution of chlorine has little effect upon starch, but when dry, starch is introduced into chlorine gas, the latter is absorbed, a little carbonic acid is evolved, the mass becomes liquid, assumes a brown colour, and is charged with much hydrochloric acid. The *bromide of starch* is an orange powder, which is formed, according to Fritzsche, when water saturated with bromine is dropt into a solution of starch in water acidulated with hydrochloric acid. The colour is destroyed by a slight heat; to obtain the *iodide of starch* in a state of purity the following process is recommended. A firm jelly is prepared by boiling potato starch with water, and after cooling, a quantity of hydrochloric acid is added sufficient to occasion the mixture to become liquid when assisted by a slight elevation of temperature. The solution is then filtered and a solution of iodine in alcohol is mixed with it, so long as the latter produces a blue precipitate, care being taken not to add too much of the solution of iodine, as the alcohol of that solution will then precipitate uncombined starch. The precipitate is collected, drained on a filter and washed with water poured upon it in small quantities. Once deprived of hydrochloric acid, the compound dissolves in the water used to wash it; the washing is therefore interrupted so soon as the liquid which passes exhibits an intense blue colour; the compound is removed from the filter and dried on a capsule over sulphuric acid in vacuo. A brown-black gummy and very brilliant mass is thus obtained, which can easily be pounded when perfectly dry, but which becomes viscous by attracting hygrometric moisture. It is very easily dissolved by water, giving a deep blue solution, and may be recovered again by evaporation in vacuo, in a dry state and without alteration. When a solution of iodide of starch is heated, it becomes colourless at 158° or 160° if very dilute, but not under 194° when the solution is concentrated. The colour reappears on the cooling of the solution, provided it has not been boiled. When the colour is not restored, the iodine appears to be converted into iodic and hydriodic acids. Animal charcoal discolours the blue solution, carrying down iodine. The iodide of starch contains 41.79 parts of iodine with 58.21 of starch, according to the analysis of Lassaigne, or it consists of two atoms of iodine with one atom of starch. (Berzelius).

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* Jacquelain, Annales de Chimie et de Physique, tome 73, p. 167.

Dextrin or mucilaginous starch.—By the action of acids, alkalies, diastase, and of heat, a complete dissolution of the gelatinous starch may be effected; it becomes largely soluble in cold water, the solution is mucilaginous and not gelatinous, and the altered starch has many of the characters of gum. Dextrin is prepared by boiling a solution of starch with a few drops of sulphuric acid, or by heating to 200°, 100 parts of starch, 20 of sulphuric acid and 28 of water, filtering and precipitating by alcohol, as a white glutinous substance becoming pulverulent by repeated washings with alcohol. It may also be prepared by diastase; an infusion of malt is mixed with a solution of starch, in the proportion of 6 or 8 of malt to 100 starch, and the liquid kept at 150° for twenty minutes. From being milky and viscid, it becomes nearly as fluid as water. It is then heated quickly to 212°, to stop the farther action of the diastase, filtered and precipitated by alcohol. The solution of dextrin was supposed not to be affected by iodine, but Jacquelain finds that dextrin is coloured purple by iodine, and not blue, like fecula, or that is not colourable by iodine, according to the circumstances of its preparation. Thus 1 part of the granules with 5 parts of water, heated to 320° for forty-five minutes, gave a dextrin which was colourable purple by iodine; while the same materials heated for one hour and forty-five minutes, at the same temperature, gave a dextrin not colourable by iodine. There can be little doubt, therefore, that there are two varieties of dextrin, *dextrin colourable by iodine*, and *dextrin not colourable by iodine*. These varieties of dextrin also appear in the succession of changes which fecula undergoes under the influence of an acid. Thus a mixture of 1 part of fecula with 1 part of water and $\frac{1}{100}$ of oxalic acid, gave when heated at 266° for twenty minutes, dextrin colourable purple, for one hour dextrin not colourable, for two hours sugar of starch also not colourable.

Dextrin is not fermentable by yeast, but is readily convertible by diastase and dilute acids into a sugar, which is fermentable. The name dextrin was applied to it by Biot from its effect upon a ray of polarised light passing through its solution, in causing the plane of polarisation to deviate very considerably to the right.* The composition of dextrin according to M. Payen, is $C_{12}H_{10}O_{10}$, and of two dextrinates of lead dried at 356°, $C_{12}H_9O_9+PbO$, and $C_{12}H_9O_9+2PbO$, so that dextrin is identical in composition with amidin, both when free and in combination. Both of the dextrinates of lead retain 1 eq. of water, when dried at inferior temperatures. A dextrinate of barytes, prepared by Payen by means of a solution of anhydrous barytes in wood spirit, and strongly dried between 356° and 374°, gave $C_{12}H_9O_9+BaO,HO$.

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* Memoirs by M. Biot, on Circular Polarisation; Taylor's Scientific Memoirs, vol. 1 pp. 584, 600, and Annales de Chimie et de Physique, tomes 69, p. 22, et 74, p. 401. When light polarised by reflection from the surface of a plate of black glass or from the surface of a pile of superposed plates of transparent glass reaches the eye through a disc of tourmalin, a solution of dextrin being interposed in a tube between the reflecting plate and tourmalin, the light does not disappear in those positions of the tourmalin in which light would be completely absorbed without the interposition of the solution of dextrin; but prismatic colours are

When dry starch is heated in an oven it becomes brown and soluble in cold water. It then forms *British gum*, which corresponds in properties with dextrin.

Diastase.—This is a remarkable substance observed by Payen and Persoz in grains and seeds, but only after germination, and in the tubers of the potato near the places from which the shoots proceed. The production of diastase is the principal object of the malting of grain or permitting it to germinate, and has an important influence upon the changes which occur in the starch of grain in brewing. Diastase is prepared by moistening freshly germinated barley with half its weight of cold water, and submitting it to pressure, by which a viscid liquid is obtained. This liquid is filtered and then heated to 158°, which causes the greater part of an azotised or albuminous matter existing in the liquid to be coagulated and separated. The liquid after filtration is mixed with a sufficient quantity of alcohol to precipitate the diastase and retain in solution the colouring matter, sugar and foreign azotised matter present. The precipitated diastase is washed with alcohol, dissolved again in water and thrown down by alcohol two several times, for the purpose of purifying it (An. de Chi. &c., liii, 73). When dried it is a white solid amorphous substance, soluble in water, but insipid, and not precipitated by subacetate of lead. It contains nitrogen, and has some analogy to gluten, but has not been obtained in a state of sufficient purity for

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produced which follow a certain order, if the plane of polarisation is turned from left to right. It is by the order of these colours, that a liquid is said to polarise light to the right or to the left. The solution of starch polarises to the right and that of dextrin considerably more so in the same direction. While a solution of cane sugar produces the succession of colours in an inverse order, and is said therefore to polarise to the left. The progress of chemical changes may thus often be observed in a solution of starch, the juices of plants and other organic fluids.

analysis. Malted barley contains not more than 1—500th of its weight of diastase. The solution of diastase has no action upon many vegetable principles, such as sugar, gum, albumen and gluten, but has a specific action upon starch, converting a solution of that substance first into dextrin, and afterwards into the sugar of starch, and such is its energy that 1 part of diastase will convert 2000 parts of starch into sugar. Diastase acts upon gelatinous starch even at 32°, but most powerfully between 140° and 150°. It has the remarkable property of separating the envelope from the grains of starch.*

In the ordinary process of brewing, the mashing or infusing of the malt should be begun at 168° or 170°, the temperature at which the diastase acts more advantageously, by which the starch of the grain is converted into sweet worts. The temperature may be afterwards raised by adding water at 185° or 195° to the mash tun; the saccharisation is generally completed in an hour and a half at the utmost, and the sweet worts are then run into a copper to be boiled and hopped, (Black on Brewing). The sugar of the cooled worts is afterwards fermented by the action of another principle yeast and converted into carbonic acid and alcohol, as will afterwards appear. The diastase of 1 part of malt is often made to succharise the starch of 10 or 12 parts of unmalted grain, when the sweet wort is to be fermented and distilled for spirits.

Gluten.—This substance remains when the starch of wheat flour has been separated by pressing the dough in water till the washings are no longer milky, as a grey viscid adhesive and elastic substance. It is insoluble in water, but is dissolved by alkalies and also by acetic acid. It contains nitrogen, and when left humid in air, has a tendency to putrify; when completely dry it is hard and brittle, with some resemblance to glue. Gluten forms from 19 to 24 per cent of good wheaten flour. According to Davy the wheat grown in the south of Europe is richer in gluten than that of colder climates; it is peculiarly suitable on that account for the manufacture of macaroni, vermicelli and similar pastes, which are made by a kind of wire drawing. Gluten is one of the most nutritive of vegetable substances; when separated however from starch and pure, gluten is scarcely digestible.

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* The name diastase was applied to it from *διιστημι*, I separate, in reference to its property of separating two supposed constituents of starch.

It is to the presence of gluten that wheat flour owes its property of forming a tenacious paste with water, and also a light spongy bread. In baking leavened or loaf bread, the dough is mixed with a quantity of yeast, or in its absence with a portion of sour dough called leaven, and set aside in a warm place, which occasions the saccharine matter of the flour to undergo the vinous fermentation. The carbonic acid gas then evolved expands the gluten into vesicles and causes the *rising* the dough, which then forms a light loaf when heated in the oven.

Gluten is not a pure principle; when digested in hot alcohol till every thing soluble is taken up, it leaves a bulky substance of a greyish colour which has been called *vegetable albumen.* The latter is soluble in water, but when the solution is heated the albumen coagulates and becomes insoluble; it is also coagulated by the stronger acids. The true gluten, obtained by evaporating the alcoholic solution, retains its adhesive property and is soluble both in acids and alkalies. It is not precipitated from a solution in acetic acid by the acetate of lead or persulphate of iron, but abundantly by the chloride of mercury and infusion of gallnuts.

Inulin.—This variety of starch was discovered by V. Rose in the root of the Inula Helenium, to which it owes its name. It is also found in various other roots, and in some lichens. It is conveniently obtained from the roots of the dahlia. The latter are rasped, washed with cold water and expressed, then boiled with water, and the hot solution filtered through linen. This solution may be clarified by white of egg, if muddy, evaporated till a pellicle forms on its surface, and then allowed to cool; the inulin is deposited in a pulverulent form. It is collected on a filter and washed well with cold water. Inulin is a very fine white tasteless powder, of density 1.336, very soluble in boiling water, but not gelatinizing, and requiring 50 parts of cold water to dissolve it. Iodine makes it yellow, and insoluble in cold water. It is insoluble in cold alcohol, soluble in acids, which change it with the aid of ebullition into sugar, and more readily than ordinary starch. It is converted by nitric acid into malic and oxalic acids, without a trace of mucic acid. It was found by Mr. E. A. Parnell, when dried at 212°, to consist of $C_{24} H_{21} O_{21}$. Two compounds which it forms with oxide of lead are thus constituted, $C_{24} H_{21} O_{21} + 5PbO$, and $C_{24} H_{18} O_{18} + 3PbO$.*

Lichen starch.—Several species of lichens, particularly the Cetraria Islandica (Iceland moss), contain a variety of starch, closely resembling common starch. It gives a white and opaque jelly. It is feebly coloured by iodine, the tint produced being between brown and green. This starch contains, according to the analysis of Guerin-Vary, $C_{10} H_{11} O_{10}$, but this result requires confirmation.

SUGARS.

Several substances are known as sugars which agree in having a sweet taste, but differ in other respects. Those which undergo a peculiar decomposition and are converted into carbonic acid and alcohol, when their solution is mixed with yeast, are fermentable sugars, and form the most important class; they are Cane sugar, Grape and Starch sugar, which appear to be identical, Milk sugar, Mushroom sugar, and the insipid sugar of Thenard, of which the two first-mentioned varieties are the most abundant and best understood.

CANE SUGAR, OR ORDINARY SUGAR,

Its formula in the crystallised state is $C_{12} H_{11} O_{11}$; in combination with oxide of lead, $C_{12} H_9 O_9 + 2PbO$ (Peligot).

Loaf sugar, sugar-candy, or the purest granular muscovado may be taken to represent this species. It exists in many plants, but is derived in large quantity only from the juice of the sugar-cane, from beet-root and the maple-tree. These juices are rapidly evaporated with a small addition of lime, to neutralise free acid, being sometimes clarified first by albumen, and afford on cooling a brown granular sugar, from which a dark coloured syrup, molasses, separates. The latter contains a portion of crystallizable sugar, which may be separated from it by evaporation, and leaves treacle, which differs in taste from crystallizable sugar, and is certainly a distinct species of sugar, although highly impure. To refine sugar, it is dissolved in water, and the solution generally filtered hot through a bed of animal charcoal in grains like gunpowder, and about two feet in thickness. The colourless syrup thus obtained is evaporated in vacuo, about 150°, in close pans heated by steam, from which the vapour is constantly withdrawn by an air-pump. When sufficiently concentrated, the syrup is run into a cooler, and agitated by an oar to promote its granulation.

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* Phil. Mag. 3rd series, vol. 17, p. 126.

It is then transferred into moulds, which are inverted cones, having an aperture in the apex, and kept in a warm place, while the dark coloured and uncrystallizable syrup drains off; a strong syrup of pure sugar being poured on the upper surface to percolate downwards and remove the last portions of the former. Instead of the pure syrup, moist pipe-clay was formerly placed on the surface of the sugar for the same purpose, and is still employed in clayed sugars. The loaf sugar from these moulds is a white compact mass, composed of small crystals. A strong solution of it, evaporated slowly, affords large transparent and colourless crystals of sugar-candy, of which the form is an oblique prism of a square base, or a six-sided prism with dihedral summits. The density of pure sugar is 1.5629 (Thomson).

Loaf sugar diffuses a phosphorescent light when broken in the dark. It is unalterable in dry air, and loses nothing but a trace of hygroscopic water when heated. It fuses at 356° (180° cent.) and forms a thick tenacious liquid, which becomes a transparent vitreous mass on cooling (barley-sugar). The latter changes after a time, and rapidly when damp, into an opaque mass, which exhibits when broken, the crystalline facets of ordinary sugar. Sugar is soluble in one third of its weight of cold, and in all proportions of boiling water. Its power to crystallise is destroyed by keeping its solution for some time boiling, and also by the addition of $\frac{1}{20}$th of its weight of oxalic, citric, or malic acid, which instantly render a viscid and boiling syrup, very fluid. Sugar dissolves in 80 parts of absolute alcohol at the boiling temperature, very slightly in the same cold, in 4 parts of alcohol of density 0.830, and is wholly insoluble in ether, which precipitates sugar from its solutions. Sugar is nutritive when accompanied with other aliments, but is incapable alone of supporting life for any length of time, in common with all organic principles destitute of nitrogen. A solution of sugar placed in contact with the stomach of the calf (rennet), is changed entirely into lactic acid, according to the observations of Fremy.

A solution of cane sugar is fermented by yeast, but not so readily as grape sugar; indeed the first action of the yeast is to convert cane sugar into grape sugar, which appears to be the only species of sugar that is directly fermentable (H. Rose); diluted sulphuric acid with heat, and tartaric acid likewise effect the latter transformation of cane sugar. The first action of caustic potash in excess upon cane sugar, at the boiling temperature, is similar. A strong syrup mixed with undiluted oil of vitriol becomes hot, swells up, much charcoal is formed, and sulphurous and formic acids disengaged. Sugar is also decomposed by hydrochloric acid, with the aid of heat, and charcoal liberated. Nitric acid converts it into saccharic, oxalic and carbonic acids, 100 parts of sugar yielding 67 parts of oxalic acid, according to Thenard. Dry chlorine has no action on dry sugar, but syrup absorbs chlorine slowly, and the sugar is converted, with disengagement of carbonic acid, into a brown matter, which retains some hydrochloric acid. Sugar dissolves carbonate of copper and verdigris, forming green solutions, which are not precipitated by alkalies; the salts, both of copper and peroxide of iron, cease to be precipitated by alkalies when sugar is added to them. Sugar also dissolves lime, barytes and oxide of lead in large quantities, and forms definite compounds with these bases, although in no respect an acid. Sugar is generally viewed as containing two atoms of water of crystallization, which cannot be expelled by heat, without destroying the sugar, but one or both of which are separated in these compounds and replaced by a metallic oxide.

Compound of sugar and lime; $C_{12} H_9 O_9 + CaO, HO$ (Peligot). When a solution of sugar is digested by a moderate heat with hydrate of lime, a bitter alkaline solution is obtained, in which 100 parts of sugar are united with 56 of lime. The compound is less soluble at a high temperature, and the solution, when boiled, becomes a thick gelatinous mass, from which the compound separates as a precipitate, and may be obtained pure by washing with boiling water, in which it is insoluble, or by precipitation with alcohol, which retains any excess of sugar. The solution of this compound absorbs carbonic acid rapidly from the air, and acute rhombohedral crystals of hydrated carbonate of lime form in it. The compound of *sugar and barytes* is similar, according to Peligot's analysis, as corrected by Liebig, or $C_{12}\ H_9\ O_9 + BaO,\ HO$. The compound of *sugar and oxide of lead*, $C_{12}\ H_9\ C_9 + PbO$, is prepared by dissolving oxide of lead in a boiling solution of sugar; it falls as a white precipitate, which is had perfectly pure by washing it with boiling water, which does not dissolve it, and drying; a soluble compound of sugar and oxide of lead is retained in the liquor which gives the precipitate. A crystalline compound of *sugar and chloride of sodium* is formed on allowing a solution of 1 part of common salt and 4 parts of sugar to evaporate spontaneously in air, the solution being decanted several times from the crystals of sugar-candy, which are first deposited. The crystals of the compound in question have a taste at once sweet and saline, and run into a liquid in humid air; their formula is $2\ C_{12}\ H_9\ O_9 + Na\ Cl,\ 3HO$:* It is probable from the composition of this salt, that the usual equivalent of sugar should be multiplied by two, if not by a higher number.

Caramel, $C_{12}\ H_9\ O_9$. At a temperature a little above its point of fusion 356°(180° cent.), sugar becomes brown, and at 410° or 428° (210° or 220° cent.) swells up and becomes a black porous shining mass, which is known as caramel, losing nothing but two atoms of water. It is obtained free from sugar, and the bitter products which accompany the caramel of the shops, by solution of the black mass in a small quantity of water, and precipitation of the caramel by alcohol, which retains the impurities in solution. Caramel is a black or very dark brown powder, neutral and insipid, soluble in water, to which it gives a fine colour of sepia, and not fermentable. It has the same composition as sugar in the compound of sugar and lead, $C_{12}\ H_9\ O_9$ (Peligot); it precipitates salts of barytes and basic salts of lead. Grape sugar furnishes the same product by heat. At a higher temperature, caramel loses more water, and forms an insoluble matter; when still more strongly heated it affords combustible gases, and leaves a bulky charcoal, difficult of incineration.

Metacetone, $C_6\ H_5\ O$ (Fremy), a combustible liquid, obtained mixed with acetone, by distilling a mixture of 1 part of sugar with 8 parts of well pulverised quick-lime. The metacetone is insoluble in water, by means of which it may be freed from acetone. It is a colourless liquid, of an agreeable odour, boiling about 183.2° (84° cent.), and miscible with alcohol and ether. It may be viewed as acetone, minus one atom of water, $C_6 H_6 O_2 - HO = C_6 H_5 O$. One atom of anhydrous sugar contains the elements of:

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* Peligot; Recherches sur la nature et les propriétés chimiques des sucres, An. de Ch. &c. t. 67, p. 113; et sur la composition du saccharate de plomb. *Ib.* t. 73, p. 103.

1 atom of acetone. . .	C_3	H_3	O
1 atom of metacetone . .	C_6	H_5	O
3 atoms of carbonic acid. .	C_2		O_6
1 atom of water. . .		H	O
	C_{12}	H_9	O_9

Saccharic acid, $C_{12} H_5 O_{11} + 5HO = C_{12} H_{10} O_{16}$ (Thaulow). This acid was designated *oxalhydric acid* by Guerin-Varry; it is a product of the action of dilute nitric acid on either cane or grape sugar. It is procured by dissolving 1 part of sugar or of gum in 2 parts of nitric acid diluted with 10 of water, and heating so long as chemical action is manifested. The acid liquid is then neutralised with carbonate of lime, and the neutral acetate of lead added to it. The saccharate of lead which falls is decomposed by sulphuretted hydrogen, and the free acid half neutralised by carbonate of potash, and crystallized as the acid saccharate of potash. The last salt is decolorized by charcoal, converted again into a salt of lead, and the acid liberated by sulphuretted hydrogen. Saccharic acid when concentrated is syrupy, colourless, sharply acid, and deposits colourless crystals, after long repose. It is soluble in alcohol in all proportions, and slightly in ether. It does not precipitate salts of barytes or lime, but produces white flocculent precipitates in barytes-water and lime-water, which are soluble in an excess of acid.

This acid is remarkable for the variety of compounds it forms with bases. It is supposed to be pentabasic, and to form 5 series of salts, according as 1 atom, 2, 3, 4, or the whole 5 atoms of water are replaced by metallic oxides; but it is possibly only tribasic, although capable of forming a subsalt with oxide of lead. Of the following salts, the composition is known

Hydrated saccharic acid . .	$C_{12}H_5O_{11}+5HO$
Acid saccharate of potash . .	$C_{12}H_5O_{11}+\begin{matrix}KO\\4HO\end{matrix}$
Saccharate of ammonia . . .	$C_{12}H_5O_{11}+\begin{matrix}NH_4O\\4HO\end{matrix}$
First saccharate of lead . .	$C_{12}H_5O_{11}+\begin{matrix}2PbO\\3HO\end{matrix}$
Saccharate of zinc	$C_{12}H_5O_{11}+\begin{matrix}2ZnO\\3HO\end{matrix}$
Second saccharate of lead . .	$C_{12}H_5O_{11}+\begin{matrix}3PbO\\2HO\end{matrix}$
Third saccharate of lead . .	$C_{12}H_5O_{11}+5PbO$

It is remarkable that hydrated saccharic acid contains the elements of 2 atoms of mucic acid; $C_{12}H_{10}O_{16}=2\ (C_6H_5O_8)$; a substance produced by the same mode of oxidation of milk sugar.*

GRAPE SUGAR.

Syn. *Starch sugar, diabetic sugar, the sugar of fruits, glucose* (Dumas). The formula of crystallised grape sugar is $C_{12}H_{14}O_{14}$, but at 212° it fuses and loses 2 atoms of water. This is the sweet principle of raisins, figs, and of most acid fruits; it exists also in honey, and is the sugar of diabetic urine. It is also a product of the decomposition or transformation of several other substances, as of cane sugar, starch, lignin and milk sugar, when treated with dilute acids. Grape sugar is not so soluble in cold water as cane sugar, and about 2½ times less sweet.

It is obtained from the grape, by neutralising the expressed juice with chalk, clarifying with white of egg, evaporating and setting aside to crystallize. From the urine of diabetes, by evaporating the latter to dryness in a water-bath, washing the dark crystalline mass on a filter with cold alcohol, and submitting the white residue, dissolved in water, to repeated crystallizations. But this sugar is most largely prepared from starch, and indeed, forms a considerable article of commerce. One part of potato starch is boiled with from 1-100th to 1-10th of its weight of sulphuric acid and four parts of water, for thirty-six or forty hours, the water being replaced as it evaporates. The solution ceases to be gelatinous, and passes first into dextrin and then into sugar. Under some pressure, and at a higher temperature, the change is effected more quickly and by means of a less quantity of acid. A small quantity of oxalic acid $\frac{1}{100}$ may be substituted with advantage in this process instead of the sulphuric acid. The acid is afterwards neutralised with chalk, the solution filtered from the insoluble salt of lime, and evaporated to a syrup, which solidifies as a crystalline sugar. Starch is also converted into sugar by means of diastase. Eight parts of ground malt are infused at 158° (70° centigrade) in 400 parts of water, and then mixed with 100 parts of starch, which soon dissolves, and by continued digestion at the same temperature is entirely changed into sugar. By calculation, 100 parts of fecula, combining with the elements of four atoms of water, should produce 122.03 parts of crystallized grape sugar; De Saussure obtained 110 parts, and Brunner from 104 to 106 parts. In the transformation of starch into sugar, a variable quality of mannite is always formed at the same time, according to the observations of Fremy.

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* Thaulow, sur l'Acide Saccharique, An: de Chimie, &c. lxix, 52.

To prepare grape sugar from lignin or woody fibre, 12 parts of wood shavings or shreds of paper are gradually mixed with 5 parts of oil of vitriol diluted with 1 part of water, care being taken to avoid any rise of temperature; after twenty-four hours' digestion, the pitchy mass is dissolved in much water, and boiled for ten hours, and the acid afterwards separated as in the former process for sugar from starch.

Grape sugar does not crystallize so distinctly as cane sugar, but is obtained from its alcoholic solution in square tables or cubes, which are hard and transparent. It is soluble in 1½ parts of cold water, and in all proportions of hot water. It dissolves less rapidly than cane sugar, and gives a more fluid syrup. In alcohol, at a low temperature, it is very sparingly soluble, but at 77° (25° cent.) it is soluble in 8 parts of alcohol of 85 per cent and in 20 parts of absolute alcohol. It fuses with loss of water at 212°, and is converted into caramel when not heated above 284° (140° cent.).

The chemical action of acids and alkalies upon grape and cane sugars are essentially different. Grape sugar dissolves in concentrated sulphuric acid, colouring it slightly yellow or brown, and forms a compound with it, the sulphosaccharic acid, while cane sugar is carbonised in the same circumstances. On the other hand, alkalies which do not alter the colour of cane sugar, even at the boiling point, provided they are dilute, convert grape sugar, with heat, into a brown or brownish black substance. The compounds of grape sugar with barytes, lime and oxide of lead are formed with difficulty, while a crystalline compound with chloride of sodium is easily prepared.

Compounds of grape sugar.—According to the recent analyses of Erdmann and Lehman, the compound of *grape sugar and chloride of sodium* contains 2 atoms of water, which it loses at 212°. Its formula in the crystallized state is $2(C_{12}H_{12}O_{12})+NaCl,2HO$. This compound loses 3 atoms of water at 320° (160° cent.), according to Peligot, but then its sugar is modified. The compound of *grape sugar and oxide of lead*, precipitated on mixing the sugar with acetate of lead containing ammonia (page 594), consists, according to the analysis of Peligot, as corrected by Liebig, of $C_{12}H_{11}O_{11}+3PbO$, or in its formation 3 atoms of water are replaced by 3 atoms of oxide of lead. The solutions of lime and barytes in grape sugar become brown, when heated.

Sulphosaccharic acid was formed by Peligot, by fusing 1 part of crystallized starch sugar by the heat of a water-bath, and then mixing the mass in small portions with concentrated sulphuric acid. The compound is then dissolved in water, and saturated with carbonate of barytes, which precipitates sulphuric acid, while the sulphosaccharate of barytes remains in solution. The acid liberated from combination is a sweet liquid, feebly acid, which forms soluble salts with almost all bases. The solution of sulphosaccharic acid is easily decomposed by evaporation, and resolved into sugar and sulphuric acid, which then precipitates barytes. Its composition has not been determined with certainty.

Sacchulmine is a substance obtained in brown, brilliant, crystalline plates, by boiling cane sugar for a very long time in very dilute sulphuric, hydrochloric or nitric acid; it is insoluble in ammonia. *Sacchulmic acid*, of which the formula is $C_{30}H_{15}O_{15}$, according to Malaguti, is formed at the same time, and many may be separated by ammonia, in which it is soluble, from sacchulmine.

Glucic acid is formed when a saturated solution of lime or barytes, in grape sugar, is left to itself for some weeks (Peligot). The probable formula of anhydrous glucic acid is $C_{24}H_{15}O_{15}$, or it is formed from grape sugar by the loss of the elements of water. *Melassic acid* is produced by the simultaneous action of alkalies and heat upon grape sugar. With the concurrence of air and a high temperature, alkalies convert sugar into formic and sacchulmic acids.

SUGAR OF MILK OR LACTINE.

Its formula, in the crystallized state, is $C_{24}H_{24}O_{24}$, or $C_{24}H_{19}O_{19}+5HO$; by a heat of 248° (120° cent.) it loses 2 atoms, and by 302° (150° cent.) 5 atoms of water (Berzelius). Sugar of milk is obtained by evaporating the whey of milk to crystallization, and purifying the first product by animal charcoal and a second crystallization. It forms white quadrangular prisms, terminated by four-sided pyramids, which are semi-transparent, and have the density 1.543. They are soluble in 5 or 6 parts of cold water, and in 2½ parts of boiling water, without forming a syrup. The sweet taste of the crystals is very feeble when they are applied directly to the tongue, but that of their solution is much more distinct. Sugar of milk is unalterable in air, loses nothing at 212°, and is insoluble in alcohol and ether. Its solution dissolves hydrate of lime, and is converted by dilute mineral acids into grape sugar, assuming then the elements of 2 atoms of water. When milk is exposed to a temperature of 95° to 104° (35° to 40° cent.), it undergoes the vinous fermentation, and is found afterwards to contain alcohol, while its sugar disappears, but the latter is converted first into grape sugar, probably under the influence of the free acid which is formed and curdles the milk. Milk sugar forms two compounds with oxide of lead, of which the formulæ are $C_{24}H_{19}O_{19}+5PbO$, and $C_{24}H_{19}O_{19}+10PbO$ (Berzelius).

Mucic acid, $C_{12}H_{8}O_{14}+2HO$ (Berzelius, Malaguti), is produced by the action of 4 parts of nitric acid, of density 1.42, diluted with 1 part of water, aided by heat, on 1 part of sugar of milk; a portion of the latter always passing at the same time into oxalic acid. It is also formed by the action of nitric acid on gum. Mucic acid is deposited on cooling, as a white crystalline powder, of which the taste is feebly acid, soluble in

6 parts of boiling water, and insoluble in alcohol. It is a bibasic acid, of which the salts of an alkaline base are soluble in water, and those which contain an alkaline earth, or the oxide of a metal proper, are insoluble. *Mucic ether*, $2C_4H_5O+C_{12}H_8O_{14}$, is solid and crystallizes in quadrilateral colourless prisms. *Modified mucic acid* is produced by boiling a concentrated solution of mucic acid, or evaporating it by heat. Its acid powers are more distinct than those of mucic acid, and it is also distinguishable from the latter by the physical properties of its salts. The modified acid is either isomeric with mucic acid, or contains the elements of an atom of water in addition (Malaguti). *Pyromucic acid*, $C_{10}H_3O_5+HO$, is produced in the dry distillation of mucic acid, by the separation of 6 atoms of water, and 2 atoms of carbonic acid;

$$C_{12}H_8O_{14}+2HO=C_{10}H_3O_5 \text{ and } 6HO \text{ and } 2CO_2.$$

It forms elongated, white and brilliant plates, which fuse at 266° (130° cent.), and volatilise without residue at a temperature a little higher. It is soluble in 26 parts of cold and in 4 parts of boiling water, dissolves easily in alcohol, and is not altered by nitric acid. It forms a class of monobasic salts, including *pyromucic ether* $C_4H_5O+C_{10}H_3O_5$, which is solid. Pyromucic ether absorbs 4 atoms of chlorine gas and becomes liquid, without the liberation of any hydrochloric acid, forming a compound, which Malaguti names *chloropyromucic ether*, $C_{14}H_8Cl_4O_6$, but of which the true constitution is uncertain.

MUSHROOM SUGAR.

This sugar, of which the formula is $C_{12}H_{13}O_{13}$, according to an analysis by MM. Liebig and Pelouze, was obtained by M. Wiggers by treating the tincture of the ergot of rye by water. It crystallizes, and is soluble in water and alcohol, but not in ether. Mushroom sugar is also fermentable by yeast, and diffuses the odour of caramel when carbonised by a high temperature. This sugar does not throw down sub-oxide of copper from a boiling solution of the acetate, the only property by which this sugar is distinguished from the ordinary species.

INSIPID SUGAR.

A species of sugar was obtained by Thenard, from the urine of diabetes insipidus, and subsequently by Bouchardat from the same source, which was insipid, or only faintly sweet. It was fermentable by yeast, and was converted by dilute sulphuric acid into the sugar of grapes.*

LIQUORICE SUGAR.

The inspissated juice of the root of the Glycyrrhiza glabra, contains a species of unfermentable sugar, which is obtained by clarifying the juice with albumen, and precipitating the sugar with sulphuric acid, washing the precipitate with water, dissolving it in alcohol, which leaves undissolved some albumen, and then decomposing the sulphate of liquorice sugar by carbonate of potash. After evaporation, the sugar remains as a yellow translucent mass, cracked in all directions, and easily detached from the vessel in which it was evaporated. Liquorice sugar possesses the property of forming soluble or sparingly soluble compounds with both the mineral and vegetable acids. It also combines with bases.

MANNA SUGAR, OR MANNITE.

$C_6H_7O_6$, according to the analyses of Oppermann and of Liebig. Manna is in oblong globules or masses, of a yellowish white colour, and is an exudation from various trees, principally the Fraxinus ornus, a species of ash, and the Eucalyptus mannifera of New South Wales. It exists also in the juices exuded by many cherry and plum trees, in various kinds of mushrooms, and in some roots, such as that of celery. It is composed chiefly of manna sugar, which may be prepared by dissolving the manna of the shops in boiling alcohol, and allowing the solution to cool, and is obtained perfectly pure by repeated crystallizations. Mannite crystallizes in slender, colourless, four-sided prisms, of a silky lustre. It has a slightly sweet taste, and is very soluble in water; its solution is not fermentable. Mannite is anhydrous, and may be fused by heat without loss of weight.

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* Thenard, Traité de Chimie, IV. 351.

Its solution dissolves oxide of lead. Nitric acid converts mannite into oxalic and saccharic acids, and not into mucic acid.

Mannite is also one of the products of the viscous fermentation of cane and grape sugar, which will be afterwards described.

GUM.

Its formula is $C_{12}H_{11}O_{11}$; it loses an atom of water at 266° (130° cent.), but is then essentially altered. Gum is a principle of constant occurrence in the juices of plants, and exuding from the bark of trees, collects into drops, which are distinguishable from resin by being soluble in water and insoluble in alcohol. All the varieties of gum may be referred to two species, of which gum-arabic (the produce of the acacia vera), and gum-tragacanth are the types. The first is slowly soluble in cold water, the last does not dissolve in water, but swells up into a mucilaginous mass, which, when boiled, gradually acquires the appearance of ordinary gum. The solution of gum, known as mucilage, is a thick, adhesive, insipid liquid, from which the gum is thrown down by alcohol. Gum is precipitated by sub-acetate of lead, as a white mass, insoluble in water. It is destroyed by the strong acids; nitric acid converts it into mucic acid.

LIGNIN.

The formula of lignin, dried between 300° and 350° is $C_{12}H_8O_8$ (Prout). The basis of woody fibre is aptly so named. It constitutes about 95 per cent of baked wood, and is the most durable product of vegetation. Pure lignin is obtained by treating the sawings of wood, paper, or the fibre of lint and cotton, successively with ether, alcohol, water, a diluted acid, and a diluted caustic alkali, to dissolve all the matters soluble in these menstrua. Wood contains in its vessels the various constituents of the sap, of which the colouring principle attaches itself to the lignin on evaporation, by a chemical affinity, such as we avail ourselves of in dyeing vegetable fibre. It has been observed by Hartig that the pores of wood also contain a certain quantity of starch, in spherical grains of a grey colour, of which from one-fourth to one-fifth of the weight of the wood may be obtained by mechanical means. The lignin of wood consists according to M. Payen, of two organic principles, which he has succeeded in separating; one is the primitive tissue, composing the vessels of the wood, which is isomeric with starch, $C_{12}H_{10}O_{10}$, and is named by him *cellulose*; the other fills the cells, and constitutes the true ligneous matter. M. Payen obtained cellulose by the action on the sawings of beech-wood of several times its weight of the most concentrated nitric acid, which leaves that principle, while it dissolves the lignin. Cellulose is dissolved by concentrated sulphuric acid, without blackening, and is then converted into dextrin. The true lignin of lint, hemp, straw, and linen cloth, was found by Payen to be $C_{35}H_{24}O_{20}$. Oak-wood, by the analysis of Gay-Lussac and Thenard, is $C_{36}H_{22}O_{22}$. Hemp, straw, etc. mixed cautiously with concentrated sulphuric acid, so as to prevent elevation of temperature, form, besides dextrine, a *lignin-sulphuric* acid, analogous to benzo-sulphuric acid, which forms soluble salts with barytes and oxide of lead. The dextrin formed when lignin is dissolved in sulphuric acid, is converted by dilution and boiling, into starch sugar. Sawdust, gum and starch dissolve in the most highly concentrated nitric acid (page 295), without decomposition of the acid, and if immediately diluted with water, give a white pulverulent neutral substance, insoluble in water, which contains the elements of nitric acid and is highly combustible (Robiquet).

Lignin combines with several neutral salts, such as chloride of mercury, sulphate of copper, and acetate of iron, with all of which, particularly the first, wood is impregnated, in order to preserve it from *dry rot*, a species of decay to which wood is subject. The wood loses all its cohesion, and becomes friable when affected by dry rot, and fungi generally appear upon it, but the first destructive change is probably of a chemical kind allied to the action of fermentation. Dr. Boucherie has found that wood may be completely charged with solutions of salts for its preservation, by aspiration from the roots or base of the trunk of the tree, shortly after it is cut down, and has made many other new observations on the subject.*

Suberic acid, $HO+C_8H_6O_3$, is formed among other products by the action of moderately concentrated nitric acid, with heat, upon barks, but more particularly cork. It is produced, likewise, from stearic and oleic acids in the same manner. Suberic acid is deposited from a saturated hot solution in water, as a white earthy powder, slightly sour, which is fusible and distils over like an oil, fixes on cooling, and is crystalline. It is soluble in alcohol and ether.

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* Annales de Chim. etc. lxxiv. 113.

SECTION II.

PRODUCTS OF THE FERMENTATION OF SUGAR.

ETHYL SERIES OF COMPOUNDS.

Ethyl, $C_4H_5{=}E$, a hypothetical radical, existing in ether and its compounds; ether being the oxide of ethyl, and alcohol the hydrated oxide of ethyl. Ethyl has not been isolated.

HYDRATED OXIDE OF ETHYL, OR ALCOHOL.

Its formula is $C_4H_5O+HO=EO+HO$. Alcohol can be obtained only in one way, namely by the fermentation of sugar, and perhaps immediately from grape or starch sugar only. This fermentation is determined by the addition of yeast to a solution of sugar kept between 70° and 80°, when a new distribution of the elements of the latter takes place, so as to form alcohol and carbonic acid; one atom of starch sugar $C_{12}H_{12}O_{12}$ being converted into two atoms of alcohol $2\ (C_4H_5O+HO)$, and four atoms of carbonic acid $4CO_2$.

Two atoms of alcohol . . .	C_8	H_{12}	O_4
Four atoms of carbonic acid .	C_4		O_8
One atom of starch sugar .	C_{12}	H_{12}	O_{12}

The juices of all plants which naturally contain sugar, possess, likewise, a substance which by exposure to air, becomes a ferment and converts their sugar into alcohol and carbonic acid. Hence all saccharine vegetable juices, such as that of the grape, of sugar-cane, and of beet-root, run quickly into fermentation after expression.

Alcohol is obtained by distillation from all liquids which have undergone the vinous fermentation, but diluted with a large quantity of water. The density of the distilled liquid diminishes with the proportion of alcohol, and tables have been constructed by which from its density the per-centage of alcohol in the liquid may be ascertained. Ordinary spirits have a specific gravity from 0.910 to 0.915, which corresponds with from 50 to 52 per cent. of alcohol. The same distilled afford a spirit of density from 0.890 to 0.880, at 60°, known as *spirits of wine*, containing from 62 to 67 per cent of alcohol; which again may be brought, by a second distillation, to from 0.843 to 0.835, known as *rectified spirits*, and these contain from 82 to 85 per cent. of alcohol.* To obtain alcohol free from water, or *absolute alcohôl*, rectified spirits may be poured into a retort over their weight of anhydrous lime, in fine powder, either fresh quick-lime finely pulverised, or better lime that has been slaked and afterwards heated recently to redness, allowed to digest together for twenty-four hours, and the spirit afterwards slowly distilled by the heat of a water-bath. It then has a specific gravity of 0.7947 at 59° (15° cent.), and from 0.792 to 0.791 at 68° (20° cent.). The *proof spirits* of the excise, upon which the duty per gallon is levied in this country, is of density 0.918633; and by the expression that a spirit is any number, say *ten, over proof*, is meant that 100 gallons of the spirit would stand the addition of ten gallons of water to reduce it to proof strength, or it would form 110 gallons of proof spirit; while *ten under proof*, means that ten gallons of water must be taken from 100 gallons of the spirit to raise it to proof, or that 100 gallons of it contain only 90 gallons of proof spirit. The proof spirit of the pharmacopæia (*spiritus tenuior*) is directed to be of sp. gr. 0.930. When obtained from grain, alcohol always contains a small quantity of a particular oil, from which it is most easily purified on the small scale by distilling it from caustic potash, or filtering it, when in a large quantity, through a bed of recently prepared wood charcoal, roughly pounded.

Alcohol has never been frozen. By evaporating the compound of solid carbonic acid and ether, in the vacuum of an air-pump, Dr. Mitchell has produced the greatest depression of temperature hitherto attained. Alcohol of specific gravity 0.798, was observed by him to become oily and adhesive at—130°;

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* Table of the Density of Alcohol, by M. Lowitz, see Appendix.

by a greater cold it became still thicker, and at—146° flowed like melted wax. Alcohol of 0.820 froze easily; ether underwent no change by the lowest of these temperatures.*

Alcohol boils at 173° (barometer 29.5 inches), and at higher temperatures, in proportion as it is diluted with water. It is remarkable, however, that the boiling point of a mixture of alcohol and water rises with the quantity of water to a certain point; alcohol of 96 to 99 per cent boiling at a somewhat lower temperature than absolute alcohol. In consequence of this, alcohol of density 0.800 is increased in strength by boiling it: and hence also, in the preparation of absolute alcohol, the first portions contain always a little more water than those which follow. Alcohol has an agreeable penetrating odour, and is the intoxicating principle of all spirituous liquors. The density of its vapour, according to Gay-Lussac, is 1613, referred to air as 1000; it contains eight volumes of carbon vapour, twelve volumes of hydrogen, and two volumes of oxygen condensed into four volumes, its combining measure, which gives the theoretical density 1601. Alcohol is highly combustible, and burns with a flame that is nearly colourless and free from smoke; the only products of its perfect combustion are water and carbonic acid.

Alcohol has a great attraction for water, which when anhydrous, alcohol attracts rapidly from the air. It also withdraws water from animal substances, and thus preserves them. When mixed with water, a very sensible evolution of heat occurs, and always a diminution of bulk and increase of density, when water and absolute alcohol are mixed in any proportions, although on adding water to alcohol, already considerably diluted, an apparent expansion may be observed. The greatest contraction occurs on mixing 1 atom of alcohol with 6 atoms of water, when a definite hydrate is certainly formed; 100 volumes of this mixture contain 53.939 volumes of alcohol, and 49.836 volumes of water; consequently, 103.775 volumes are reduced to 100; its density is 0.927 at 59°.†

Alcohol dissolves most of the gases, and several of them in a larger proportion than water, such as oxygen, nitrous oxide, carbonic acid, and phosphuretted hydrogen. It dissolves the hydrates of potash and soda, ammonia, the alkaline sulphurets, likewise all the deliquescent inorganic salts, except carbonate of potash, but none of the salts which are insoluble or sparingly soluble in water, nor efflorescent salts. It dissolves many vegetable principles, such as sugar, resins, essential oils, soap, castor oil, ethers, alkalies, most acids, &c. It does not dissolve the fats and fixed oils. Alcohol forms crystalline compounds with several of the salts it dissolves, particularly chloride of calcium, ($CaCl+2C_4H_6O_2$), nitrates of lime and magnesia, chloride of zinc, and chloride of manganese. These compounds are named *alcoates*, and correspond with hydrates, but are much less stable. Many solutions made by alcohol, or *tinctures*, are used in medicine.

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* Liebig's Annalen, vol. 37, p. 354; from Silliman's American Journal of Science.

† Rudberg, Annales de Chim. etc. xlviii, 33.

Absolute alcohol dissolves 1-240th of phosphorus, and 1-200th of sulphur. It is decomposed by potassium or sodium, with the evolution of hydrogen gas, and a crystallizable compound is formed of the remaining elements of the alcohol with the metal, or perhaps of ether with the oxide of the metal. This substance is decomposed by water. Oxygen acids decompose alcohol, as they do a hydrated metallic oxide, uniting directly with the ether it contains, and forming acid salts of that base; while a hydracid acts upon the ether of the alcohol as it does upon a metallic oxide, forming water, and a haloid compound of the radical of the hydracid with ethyl.

OXIDE OF ETHYL, OR ETHER.

Formula: $C_4H_5O=EO$; distinguished also as *sulphuric ether*, from the mode of preparing it. This liquid is the product of a remarkable decomposition of alcohol by sulphuric, phosphoric and arsenic acids, and is also formed by the action upon alcohol of the fluoride of boron, the chloride of zinc, the chloride of tin, and some other chlorides. All these agents have a great affinity for water, and might be supposed to convert alcohol into ether by simply combining with the water which the former is supposed to contain, but the close examination which the process of etherification has received from chemists, proves that its rationale is by no means so simple. Reserving the theory of ether till that of sulpho-vinic acid is considered, I shall at present describe the process for ether.

Ether is evolved when alcohol and oil of vitriol are heated together, and may be obtained by mixing and distilling in a glass retort equal weights of these materials, due attention being paid to the condensation of the product, which is volatile, by keeping the receiver very cold. But as the power of the acid to decompose alcohol is not exhausted in this process, it is found advantageous to make additions of alcohol to the remaining acid, or to introduce the latter in a continued stream. The following is a *continuous process* for ether, first proposed by M. Mitscherlich, as it is given by M. Liebig. Alcohol is employed of density 0.822, or of 90 per cent. which may be obtained by digesting proof spirits upon an equal weight of well dried carbonate of potash (free from caustic potash), when two liquids are formed, the upper alcohol of the strength mentioned, which may be drawn off for use, and the lower, a solution of carbonate of potash in water. Five parts, by weight, of this alcohol are mixed with nine parts of oil of vitriol, in a copper or cast iron vessel, surrounded by cold water, and the mixture afterwards introduced into a tubulated glass retort, which the mixture should fill one half, or even a little more. The distillation is best conducted by the heat of a sand-pot, in which the retort should not be deeply sunk, and commences at a gentle heat; when the temperature increases too briskly, the fire should be withdrawn. A glass tube is fixed by a cork in the tubulure of the retort, of which the extremity within the retort is drawn out into a point, having an opening about one line in diameter, and dips one inch in the liquid. Without the retort, the same tube is bent at a right angle, and may extend horizontally for two or three feet; it communicates with a reservoir of alcohol by means of a metallic tube and stop-cock, by which the flow of the alcohol is regulated. The latter should be supplied so as to keep the liquid in the retort at its original level, at which a mark should be placed for that purpose. To condense the ether which distils over, the beak of the retort is connected with Liebig's tube condenser, charged with the coldest water. A leaden alembic is used when ether is prepared on a large scale. It is said that when operation is well directed, nothing is formed but ether and water; the same sulphuric acid may also be used indefinitely for the preparation of ether without sensibly diminishing, the ether and water into which the alcohol is resolved, coming off entirely, and leaving none of its elements with the acid.

To obtain the ether perfectly free from alcohol and other impurities, the crude product may be mixed with some milk of lime and an equal volume of water, the lighter liquid drawn off, and allowed to digest for several days upon chloride of calcium, or quicklime; and finally be rectified from the same substances. The last product has a specific gravity between 0.720 and 0.725.

Ether is a light, transparent, highly limpid, fragrant and volatile liquid, having a sharp aromatic taste, and which when swallowed or inhaled in the form of vapour, acts as a powerful stimulant. Its density is 0.715 at 68°, and 0.724 at 54°, by Gay-Lussac's observations. It boils between 96° and 98° (26°.5 cent. Gay-Lussac); evaporates rapidly at ordinary temperatures, and produces great cold by its evaporation. It is very combustible, and a mixture of its vapour with air or oxygen is explosive in a high degree; hence it must always be distilled with caution. Ether, unlike alcohol, burns with a white flame; it is converted into water and carbonic acid. When a spiral coil of platinum wire, heated red-hot, is suspended in the vapour of ether, the latter burns without flame, and produces a very acrid vapour, which when condensed has been found to contain acetic, formic and aldehydic acids. When transmitted through a red hot tube, ether is decomposed into aldehyde, olefiant gas, and the gas of marshes.

Ether mixes with alcohol in all proportions, but may be separated completely from the latter by agitation with twice its bulk of water, which takes up the alcohol while the ether floats on its surface. One part of ether dissolves in 10 parts of water, while 36 parts of ether dissolve 1 of water. Its solvent powers are much less extensive than those of alcohol. Ether dissolves 1-80th of sulphur, and 1-37th of phosphorus, and also iodine and bromine in large quantity, but is soon decomposed by them. It dissolves also a considerable number of chlorides, such as that of mercury, of zinc, and gold. Ether dissolves also several organic acids, such as the acetic, gallic, benzoic, oleic and stearic acids, also the essential oils, fats, wax, and certain resins. Certain vegetable bases are also soluble in ether, while others are not.

The vapour of ether is very heavy, its density being 2586 (Gay-Lussac); it contains 8 volumes of carbon vapour, 10 volumes of hydrogen, and 1 volume of oxygen, condensed into 2 volumes, which form its combining measure, and give as its theoretical density 2583.

Ether left a long time in contact with water, combines with it and forms alcohol. It combines with acids, and forms both neutral and acid salts; the first class of salts are the compound ethers, and the last bear the name of vinic acids.

CHLORIDE OF ETHYL, OR HYDROCLORIC ETHER.

Its formula is $C_4H_5Cl{=}ECl$. To prepare this ether, alcohol is saturated with hydrochloric acid gas, and the solution distilled by a water-bath heat; the product is conducted into a bottle containing some water and surrounded by water at the temperature of 70° or 80°, and thence into another receiver surrounded by ice. To free it from water and alcohol, the product is digested with chloride of calcium in a bottle surrounded by ice. The liquid is decanted, after twenty-four hours, into phials, with well ground stoppers, which are kept inverted.

Hydrochloric ether is a highly volatile liquid, boiling at 52°, of a penetrating aromatic and slightly alliaceous odour. Its density is 0.874 at 41°, it is neutral to test paper, dissolves in twenty-four parts of water, and gives a solution that is not precipitated by nitrate of silver. When treated with chlorine, it gives hydrochloric acid, and a series of compounds to which reference has already been made (page 718).

Bromide of ethyl, $C_4H_5Br{=}EBr$, was discovered by Serullas, and is formed by distilling a mixture of 1 part of bromine, 4 of alcohol, and 1-8th of phosphorus. It is a colourless and very volatile liquid, denser than water.

Iodide of ethyl, $C_4H_5I{=}EI$, may be obtained by distilling alcohol, saturated with hydriodic acid gas. It is a colourless liquid, of density 1.9206, which boils at 161°. (71°. 5 cent.)

Sulphuret of ethyl, $C_4H_5S{=}ES$, is formed by transmitting the vapour of hydrochloric ether through the proto-sulphuret of potassium; chloride of potassium precipitates, the sulphuret of ethyl is dissolved by the liquid, or distils over if the latter is kept warm. It is a colourless liquid, of a disagreeable alliaceous odour, boiling at 163°.4 (73° cent.), and of which the density is 0.825 at 68°.*

HYDROSULPHURET OF THE SULPHURET OF ETHYL, OR MERCAPTAN.

Its formula is $C_4H_5S+HS=ES+HS$; or it is alcohol of which the oxygen is replaced by sulphur. This curious compound, of which we owe the discovery to Zeise, may be prepared like the preceding compound, by transmitting the vapour of hydrochloric ether through a strong solution of potash, previously saturated with sulphuretted hydrogen gas, or hydrosulphuret of sulphuret of potassium, $KS+HS$; but a preferable process is to distil a strong solution of the sulphate of oxide of ethyl and lime, of density 1.28, mixed with a solution of potash of the same density, previously saturated with sulphuretted hydrogen gas.

$$KS, SH \text{ and } (EO+CaO+2SO_3)=ES+HS \text{ and } KO+SO_3 \text{ and } CaO+SO_3.$$

The product must be received in a cool receiver. It contains an excess of sulphuretted hydrogen, alcohol, and water, from which it may be purified by submitting it to a second distillation from a small quantity of red oxide of mercury, and digesting it afterwards with chloride of calcium.

Mercaptan is a colourless liquid, highly fluid like ether, having a most penetrating and insupportable garlic odour; its boiling point is about 100°, according to my own observation, and the density is said to be 0.835 at 70°, and 0.842 at 59°. It is miscible with alcohol and ether, but not with water, in which it is very slightly soluble. The sulphuretted hydrogen of mercaptan acts powerfully on metallic oxides, water being formed, and a sulphuret of the metal, which last remains in combination with the sulphuret of ethyl, thus forming a class of sulphur salts. The oxide of mercury is instantly converted by mercaptan into a compound of this class, C_4H_5S+HgS,† the *mercaptide of mercury*, which is a white crystalline mass, soft to the touch, without odour, insoluble in water, and fusible like wax by 185° (85° cent.). This mercaptide, when distilled, leaves cinnabar, and affords a volatile liquid, which has not been examined. The oxide of gold is also strongly acted on by mercaptan, but other metallic oxides are less affected in proportion as they approach to alkaline bases. Thus the hydrates of potash and soda have no sensible action on mercaptan.

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* Regnault, An. de Ch. etc. lxxi, 387.

† Hence the name mercaptan, from *mercurium captans*.

By contact with nitric acid, mercaptan is converted, by a gentle heat, into a new acid, which contains sulphuret of ethyl and the elements of sulphuric acid, $C_4H_5S_2O_2$. (Lœwig, Kopp).

Bisulphuret of ethyl, $C_4H_5S_2=ES_2$, is a transparent oily liquid, boiling at 123.8° (51° cent.), obtained by distilling a mixture of the double sulphate of ethyl and potash and the persulphuret of potassium. It is decomposed by caustic potash and by nitric acid (Zeise, Pyrame Morin).

Seleniuret of ethyl, is obtained, according to Lœwig, in the same way as the sulphuret, substituting in the process seleniaret of potassium for the sulphuret of potassium.

Telluret of ethyl, obtained also by a similar process, using the telluret of potassium; a very volatile liquid, of a deep orange colour (Wœhler).

Cyanide of ethyl, hydrocyanic ether, $C_4H_5+NC_2=ECy$, obtained by Pelouze by exposing a dry mixture of sulphate of ethyl and potash to a gentle heat, which is gradually increased. It is a colourless liquid, with an insupportable odour of garlic, boiling at 179.6° (82° cent.), and of which the density is 0.7. *Sulphocyanide of ethyl* has also been formed by distilling a mixture of sulphocyanide of potassium, alcohol and sulphuric acid. It is an oily, very dense liquid.

SALTS OF OXIDE OF ETHYL, OR SALTS OF ETHER.

Ether does not combine directly with acids, but these salts are obtained by the action of acids upon alcohol (hydrate of ether). The neutral salts of ether are distinguished from inorganic salts by the circumstance that neither the acid nor oxide of ethyl can be replaced by double decomposition, at the ordinary temperature, by another acid or base, when the salt of it is mixed with another salt; the alcoholic solution of the oxalate of ether, for instance, not being precipitated by an alcoholic solution of chloride of calcium. These salts are decomposed by the alkaline hydrates, particularly when assisted by heat, their base attaching itself to the water of the alkaline hydrate, and coming off as alcohol, while their acid unites with the alkali. Several of these neutral salts are only partially decomposed by alkalies and metallic oxides, a neutral double salt being formed, in which the acid is united with equal proportions of oxide of ethyl and metallic oxide. The latter can again be removed by a stronger acid for which it has an affinity, and then an acid double salt is formed, in which the ethyl is combined with a salt of water. The metallic oxide of the neutral double salts can also be replaced by another metallic oxide, but the acid of the double salt is not affected by its usual precipitants, the sulphate of ethyl and potash, for instance, not being precipitated by chloride of barium.

The acid salts of oxide of ethyl are not crystallizable, a concentrated solution has a certain degree of stability, and may be heated to 212°, but a dilute solution decomposes spontaneously at the temperature of the air, and more rapidly when heated, with the formation of alcohol and a hydrate of the acid. Some of them, of which the hydrate is but slightly volatile, such as the acid sulphate of ether, are decomposed at a higher temperature into ether which escapes and acid which remains in the state of hydrate.

The neutral salts of ethyl are generally derived from the acid sulphate of ethyl. When to a highly concentrated solution of the latter, solutions of other acids are added, it usually happens that the latter assume the oxide of ethyl to form neutral salts, and leave behind the hydrate of sulphuric acid; the mucate, oleate and stearate of ethyl are formed in this way. Or when to a similar solution of the acid sulphate of ethyl salts are added, of which the acids are volatile and form volatile compounds with oxide of ethyl, the sulphuric acid unites with the base of the other salt, while the volatile acid combines with oxide of ethyl, and distils over with the latter.

ACID SULPHATE OF OXIDE OF ETHYL, OR SULPHATE OF OXIDE OF ETHYL AND WATER.

Syn. *Etherosulphuric acid, sulphethylic acid* (Mitscherlich), *sulphovinic acid*; $EO,SO_3 + HO,SO_3$.

The neutral sulphate of ethyl has not yet been formed.

The acid sulphate of ethyl may be formed directly by transmitting the vapour of ether through the hydrate of sulphuric acid so long as it is dissolved. On afterwards diluting that liquid with water, part of the ether separates in a free state, and part remains in combination with the acid.

The same compound, however, is obtained from the action of sulphuric acid on alcohol, a chemical action which cannot yet be said to be fully explained, although it has been the subject of much research. There are two steps in this action: 1. the production of sulphovinic acid, and 2. the liberation of ether.

1. *Formation of sulphovinic acid.*—Equal weights of strong alcohol and oil of vitriol heated together to the boiling point of the mixture, and saturated at that temperature with milk of lime, give the sulphovinate of lime, or sulphate of ethyl and lime, which is soluble and may be separated by filtration from a considerable quantity of insoluble sulphate of lime, which is always formed at the same time. It is observed that the cooling and the dilution of the mixture of alcohol and sulphuric acid, before saturation, diminishes the proportion of sulphovinic acid, or of sulphovinate of lime formed, by causing a reproduction of alcohol. Even when the sulphuric acid is in great excess, a considerable proportion of alcohol, often nearly the half of it, escapes decomposition, or is not found in the sulphovinic acid when neutralised. That the whole alcohol, however, is at first converted into sulphovinic acid appears from the circumstance that the mixture is not decomposed by a current of dry chlorine, no hydrochloric being formed, a property of sulphovinates, which undergo no modification by the action of chlorine, while free alcohol is immediately decomposed into hydrochloric acid and other chloruretted products. A mixture of 100 parts of oil of vitriol, 48 parts of alcohol, and 18.5 parts of water, which contains the elements of 2 atoms of sulphuric acid, 1 atom of ether, and 6 atoms of water, boils at 284° (140° cent.), and is not affected by chlorine; it may be represented as $(EO,SO_3+HO,SO_3)+5HO$.

The protohydrate of sulphuric acid, diluted with 55 per cent. of water, or HO,SO_3+3HO, does not decompose alcohol at the ordinary temperature, but the reaction occurs when the mixture is boiled.

It is observed by Mitscherlich that in the formation of sulphovinic acid, there is only a feeble disengagement of heat. If to two parts of alcohol, one part of sulphuric acid and then one part of water be added, the temperature of the mixture rises to 518° (70° cent.); about half of the alcohol being converted into sulphovinic acid. While if to one part of sulphuric acid, one part of water be first added, and then two parts of alcohol, the temperature rises to 154.4° (86° cent.), or nearly as high, although in the last case no sulphovinic acid is formed. Consequently the heat evolved when sulphuric acid unites with oxide of ethyl is scarcely superior to that liberated when the protohydrate of sulphuric acid unites with more water.*

2. *Formation of ether.*—A mixture of 9 parts of hydrated sulphuric acid and 5 parts of alcohol of 85 per cent which is heated to the boiling point for ether, contains the elements exactly of 1 atom of the acid sulphate of ether, and 3 atoms of water, or $(EO,SO_3+HO,SO_3)+3HO$. When this mixture is heated above 284°, the acid sulphate of oxide of ethyl is decomposed into ether and water, which distil over very nearly if not exactly in the proportions in which they exist in alcohol. The escape of ether from this mixture is not promoted by the addition of strong sulphuric acid to it, but, on the contrary, retarded, and then requires a higher temperature. On the other hand, more alcohol added to the mixture distils off undecomposed in the anhydrous state. The water present in the ether mixture is necessary, and must act as a stronger base, displacing the oxide of ethyl in combination with the acid, and liberating it as ether (page 188). Water may even displace so strong a base as ammonia, when assisted by the volatility of the latter; a solution of the neutral sulphate of ammonia becoming acid when boiled for some time, from the escape of ammonia (Rose). The addition, however, of more water to the ether mixture above, so as to lower its boiling point below 258.8° (126° cent.), occasions the destruction of the sulphovinic acid, and then nothing but alcohol distils over.

It was observed by Rose that ether begins to be slowly evolved from the ether mixture, at a temperature scarcely amounting to 212°; the ether is nearly pure, the water of the alcohol being retained at that temperature by the sulphuric acid.‡ Liebig finds that on directing a current of dry air through the ether mixture heated to 284°, the point of ebullition falls to 273.2° (134° cent.), and on examining what was carried away by the air, it was found to be nothing but alcohol.* The evolution of ether does not indeed proceed well, unless with a regular ebullition of the liquid.

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* L'Institut, No. 390, page 206; 17 Juin, 1841; where etherification and other theoretical questions are discussed by M. Mitscherlich.

‡ H. Rose on Etherification, Taylor's Scientific Memoirs, vol. ii.

When the ether mixture contains a great excess of sulphuric acid, the decomposition of the sulphate of oxide of ethyl does not take place till the temperature rises to 320^0 (160^0 cent.), and then a variety of products are evolved, which Liebig refers to the re-action of the elements of sulphuric acid themselves upon oxide of ethyl. He supposes the elements of 1 atom of the acid sulphate of oxide of ethyl to divide themselves in the following manner:

2 eq. of sulphurous acid	$S_2 \quad O_4$
½ eq. of olefiant gas	C_2H_2
3 eq. of water	H_3O_3
2 eq. of carbon, as residue . . .	C_2
	$S_2C_4H_5O_7$

This appears to represent pretty well the decomposition by which olefiant gas is usually obtained (page 426); but that gas may be obtained, according to Mitscherlich, accompanied by nothing but water, when sulphuric acid is diluted with water so as to boil at 320^0, and the vapour of alcohol containing 20 per cent of water (density 0.844) is sent through it. After a part of the water is expelled by the heat, bubbles of olefiant gas appear in all parts of the liquid. The gas is accompanied by very little ether, and by almost no acid body; and the liquid, even after it has produced a cubic foot of olefiant gas remains colourless, without any deposit of carbon. The other substances obtained in the ordinary preparation of olefiant gas, Mitscherlich considers as secondary products, which only begin to be formed when with alcohol of 80 per cent a temperature is employed of 338^0 (170^0 cent.).

In the ordinary decomposition of alcohol for olefiant gas, there is also formed a small quantity of the double sulphate of oxide of ethyl and etherole (oil of wine). The carbonaceous residue has also been shown not to be pure carbon, but a compound substance, and named *Thiomelanic acid* by Erdman. Its composition in its potash salt is $C_{80}H_{24}S_3O_{20}+2KO$.

The solution of the acid sulphate of oxide of ethyl is a liquid of a very sour taste; when diluted it cannot be concentrated by evaporation at any temperature without decomposition. It is obtained in a state of perfect purity by heating slightly the sulphate of ethyl and etherole in contact with 4 parts of water; the etherole (light oil of wine) separates and comes to the surface, while the acid sulphate of ethyl dissolves in the water. It forms a great number of double salts with bases, which to 2 atoms of sulphuric acid contain 1 atom of oxide of ethyl, and 1 atom of the base added. They are soluble in water, and in alcohol which is not anhydrous; their sulphuric acid cannot be detected by the usual re-agents, but on boiling their solution with a few drops of hydrochloric acid, alcohol is disengaged, and thereafter the presence of sulphuric acid can easily be detected in the residue. They are not decomposed by a current of gaseous chlorine; the potash and soda salts are not decomposed when boiled with an excess of these alkalies; the barytic salt distilled with sulphuric acid containing 4 atoms of water gives a mixture of ether and alcohol; concentrated solutions of all of them are gradually decomposed by ebullition. When a sulphovinate is submitted to dry distillation with hydrate of lime or barytes, it is converted into a neutral sulphate and alcohol.

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* Traité de Chimie Organique, tome i, page 334.

The sulphovinate of potash is the only anhydrous salt, all the others contain water of crystallization, which they generally lose when dried in vacuo at the ordinary temperature. The salts of potash, soda, and ammonia are prepared by precipitating the double sulphate of ethyl and lime or the salt of barytes, by the alkaline carbonates; the double sulphate of ethyl and magnesia or manganese, by decomposing the double sulphate of ethyl and barytes, by means of soluble sulphates.

These salts have all more the character of a bibasic salt, than of a double sulphate or compound of two monobasic sulphates, and may therefore be represented as containing a sulphuric acid of double atom S_2O_6, which is bibasic, and is united at once with oxide of ethyl and another base, of which the last only can be displaced by other bases. They resemble the bibasic fulminate of silver, in which one atom only of base can be displaced by another base.

Sulphate of oxide of ethyl and potash, $KO,EO+S_2O_6$, crystallizes in colourless plates like chlorate of potash, which have a saline and sweetish taste; is persistent in air, soluble in an equal weight of water, also in dilute alcohol, but insoluble in anhydrous alcohol and ether; above 212° it undergoes decomposition without entering into fusion.

Sulphate of oxide of ethyl, and barytes, $BaO,EO+S_2O_6+2HO$, crystallizes in plates or rhomboidal prisms, persistent in air, and having a very acid taste.

Sulphate of oxide of ethyl, and lime, $CaO,EO+S_2O_6+2HO$. Five parts of this salt dissolve in 4 parts of water at 62.6 (17° cent.); it is also soluble in alcohol with the aid of heat.

Sulphate of oxide of ethyl, and oxide of lead, $PbO,EO+S_2O_6+2HO$, crystallizes in large transparent tables, very soluble both in water and alcohol, and having an acid re-action. It slowly undergoes spontaneous decomposition, and becomes viscid from the formation of oil of wine. It dissolves an additional atom of oxide of lead, and becomes a *basic salt,* which becomes a white mass, and is very soluble.

Acid phosphate of oxide of ethyl, phosphovinic acid, $2HO,EO+PO_5$, is formed on mixing alcohol with a concentrated solution of phosphoric acid, with the evolution of much heat; if the phosphoric acid is diluted so that its density does not exceed 1.2, it is not in a state to decompose alcohol. Phosphovinic acid is a colourless, syrupy liquid, of an acrid and very acid taste, more stable than sulphovinic acid, as it may be boiled without decomposition, even when diluted. At a higher temperature it is decomposed, giving first ether and alcohol, then inflammable gases and a carbonaceous residue. When phosphovinic acid is treated with metallic oxides, the two atoms of basic water which it contains are separated and replaced by fixed base, while the oxide of ethyl remains, a tribasic class of salts being formed like the ordinary phosphates. The formula of the *phosphate of ethyl and barytes* is $2BaO,EO+PO_5+12HO$. The compounds of pyrophosphoric acid and metaphosphoric acid with oxide of ethyl have not yet been obtained (Pelouze).

Arseniate of oxide of ethyl, arseniovinic acid,* $HO,2EO+As\,O_5$, contains 2 atoms of oxide of ethyl and 1 atom of basic water, which last may be replaced by fixed bases (D'Arcet).

Nitrite of oxide of ethyl, nitrous ether, $C_4H_5O+NO_3=EO,NO_3$. Nitric acid decomposes alcohol without combining with it. This ether may be obtained, however, by distilling 3 parts of strong alcohol with 2 parts of nitric acid of density 1.3, applying occasionally a very gentle heat, and condensing in a receiver surrounded by ice. But as prepared with nitric acid, by this and other processes, nitrous ether always contains aldehyde, a product of the oxidation of alcohol. M. Liebig recommends as the best process for nitrous ether, to transmit a current of nitrous acid vapour, obtained by heating on a water-bath a spacious retort, containing 1 part of starch and 10 parts of nitric acid of 1.3, through a mixture of 2 parts of alcohol of 85 per cent and 1 part of water, contained in a bottle of two tubulures, and surrounded by cold water. The nitrous acid is immediately absorbed by the alcohol, and combines with ether. The product, at the same time, distils over, and may be conducted from the vessel in which the reaction takes place, by means of a glass tube, to a tube condenser.

Nitrous ether, in a state of purity, is a volatile liquid, of a pale yellow colour, possessing the agreeable odour of the Normandy rennet. Its density at 59^0 (15^0 cent.) is 0.947; it boils at 61.5^0 (16.4^0 cent.). It is converted by the tincture of hydrate of potash into nitrate of potash and alcohol.

Carbonate of oxide of ethyl, carbonic ether, EO,CO_2; obtained by M. Ettling, by the action of potassium or sodium on oxalic ether; a colourless aromatic liquid, of density 0.965 at 66.2^0 (19^0 cent.), boiling at 258.8^0 (126^0 cent.).

Carbonate of oxide of ethyl and potash, $KO,EO + C_2O_4$; is prepared by dissolving in alcohol hydrate of potash, fused and still red hot, and saturating the solution with dry carbonic acid gas. When purified, it crystallizes in silky laminæ, soft to the touch (Dumas and Peligot).

Oxalate of ether, oxalic ether, EO,C_2O_5. The following process is given by M. Liebig, from Ettling, for the preparation of this which is one of the most interesting of the ethers. A mixture is distilled rapidly of 4 parts of binoxalate or quadroxalate of potash, 5 parts of oil of vitriol, and 4 parts of alcohol of 90 per cent (0.818). As soon as the liquid which passes is troubled by an addition of water, it contains oxalic ether, and is collected in a receiver which is not cooled. The product is afterwards mixed with 4 times its volume of water; the ether then separates, and it is agitated immediately with pure water, which is renewed frequently, till an acid re-action ceases to be manifested.

The washed ether is rectified in a small dry retort, which is filled to 9-10ths; as soon as the product which passes is colourless and transparent, and the liquid boils tranquilly in the retort without bumping, it is necessary to change the receiver, for from that period the oxalic ether distils over, pure and anhydrous. The residue in the retort contains some traces of oxalic acid. (Traité, p. 350).

Oxalic ether is a colourless liquid, of an aromatic odour; its density 1.0929, and boiling point 363.2° (180° cent.). When pure it may be kept in contact with water for several days without decomposition, but if it contains the smallest trace of acid or alcohol, it is decomposed rapidly into oxalic acid and alcohol. The fixed alkalies act upon it in the same manner as water.

By ammonia or solution of ammonia in excess, oxalic ether is instantly decomposed, a beautiful white precipitate of *oxamide* (page 407) appearing and alcohol is reproduced:

$$NH_3 \text{ and } EO,C_2O_5,=NH_2,C_2O_4 \text{ (oxamide) and } EO,HO \text{ (alcohol).}$$

Oxalate of ether and oxamide, or oxamethane; $EO,C_2O_5+NH_2,C_2O_4$; or $C_8H_7NO_6$, is a substance in beautiful white crystalline leaflets, formed by adding alcohol saturated with ammoniacal gas to a solution of oxalic ether in alcohol. It is fusible about 212°, distils at 428° (220° cent.) without alteration. Four atoms of the hydrogen of this compound can be replaced by chlorine, and *chloroxamethane* formed, $C_8\begin{matrix}H_3\\Cl_4\end{matrix}NO_6$, which strikingly resembles oxamethane in its physical properties, and is even believed to be isomorphous with it.

Oxalate of oxide of ethyl and potash, oxalovinate of potash, $KO,EO+C_4O_{10}$. This salt is prepared by adding to a solution of 1 volume of oxalic ether in 2 volumes of alcohol, somewhat less than half the potash dissolved in alcohol, which would be required to form a neutral salt with the oxalic acid of the ether; the salt precipitates, being insoluble in the alcohol. It is anhydrous.

Acid oxalate of oxide of ethyl and potash, oxalovinic acid, $HO,EO+C_4O_{10}$, is obtained by treating an alcoholic solution of the preceding salt with hydrofluosilicic acid, or by decomposing with caution an aqueous solution of the oxalate of ethyl and barytes by dilute sulphuric acid. It is a very acid liquid, which is decomposed by evaporation.

Sulphocarbonate of oxide of ethyl and potash, xanthate of potash *of Zeise*; $KO,EO+C_2S_4$. This salt contains 2 atoms of bisulphuret of carbon, united with 1 of potash and 1 of oxide of ethyl. It is formed on pouring the bisulphuret of carbon into absolute alcohol saturated cold with hydrate of potash, and keeping the mixture at a gentle heat; the liquor becomes a crystalline mass of the salt at 32°. The salt crystallizes in colourless or yellowish crystals.

Sulphocarbonate of oxide of ethyl and water or *xanthic acid*, $HO,EO+C_2S_4$, is obtained as an oily liquid, insoluble in water, when the preceding potash salt is decomposed by dilute sulphuric or hydrochloric acid.

Bicyannurate of oxide of ethyl, cyanic ether, $3EO+2Cy_3O_3+6HO$. This compound was obtained by Liebig and Wœhler by directing the vapours of hydrated cyanic acid into a mixture of alcohol and ether, as long as they were absorbed. The compound crystallizes after twenty-four hours' repose, and is purified from cyamelide, with which it is accompanied, by solution in boiling alcohol or water and a second crystallization. Its solution is neutral to test paper, and it does not form compounds with metallic oxides.

Benzoate of oxide ethyl, benzoic ether, $C_4H_5O+C_{14}H_5O_3=EO,BzO$. This is a liquid ether, of density 1.0539 at 50° (10° cent.), boiling at 408.2° (210° cent.), prepared by distilling a mixture of 4 parts of alcohol of 83 per cent. (0.840) with 2 parts of crystallized benzoic acid, and 1 part of concentrated hydrochloric acid.

Hippurate of oxide of ethyl, hippuric ether, $C_4H_5O+C_{18}H_8NO_5$. This compound was first prepared by Dr. Stenhouse. It is obtained in fine crystalline needles, perfectly white, and of a silky lustre. The crystals are not volatile, their density is 1.043 at 73.4° (23° cent.); they fuse at 109.4° (43° cent.)

Chloroxi-carbonic ether, $C_4H_5O+C_2O_3Cl$. This name has been given by M. Dumas to an ethereal liquid, which is formed when absolute alcohol is brought into contact with chlorocarbonic acid gas (page 378). Its density is 1.33 at 59°; it boils at 201.2° (94°cent.).

Urethane, $C_6H_7O_4N$. This substance is formed, with sal ammoniac, on dissolving the preceding compound in solution of ammonia. Purified by distillation, it is a pearly-white, crystalline substance, resembling spermaceti; it fuses at 212°, and distils without change at 356° (180° cent.). Urethane may be considered as a chloroxicarbonic ether, in which the chlorine is replaced by amidogen, $C_4H_5O + C_2O_3$ (NH_2). It may also be looked upon as the product of the combination of 2 atoms of carbonic ether with 1 atom of urea, $2C_5H_5O_3 + C_2O_2, N_2H_4$, the consideration which induced M. Dumas to give it the name of urethane.

Some other compound ethers or neutral salts of oxide of ethyl will be described under their respective acids.

TRANSFORMATIONS OF THE BODIES CONTAINING ETHYL.

The compound of alcohol and chloride of zinc was found by M. Masson to give ether and water when heated to 284°, and at a higher temperature, between 320° and 392°, two *liquid hydrocarbons*; one boiling at 212° represented by C_8H_7, and the other boiling at 572° (300° cent.) C_8H_9; the sum of which is $C_{16}H_{16}$, exactly the composition of olefiant gas. The liquid long known as *oil of wine* is probably one of these hydrocarbons. It is found in the retort from which a considerable quantity of crude ether has been distilled off lime.

Sulphate of oxide of ethyl and of etherole, $C_4H_5O, C_4H_4 + S_2O_6$, long known as the *sweet oil of wine* or the *heavy oil of wine*. This compound arises from the decomposition of the neutral sulphate of oxide of ethyl, which cannot exist in an isolated state, and is best obtained by distilling 3 atoms of the sulphovinate of lime with 1 atom of caustic lime; these give 1 atom of sulphate of oxide of ethyl and etherole, 1 atom of alcohol, and 4 atoms of sulphate of lime. The sulphate of oxide of ethyl and of etherole is a colourless oily and aromatic liquid, of density 1.33, boiling at 536° (280° cent.), and capable of being distilled without alteration, if free from water. It is decomposed by water and by acids into sulphovinic acid and etherole. *Etherole*, first observed by Mr. Hennel, and sometimes called the *light oil of wine*, is an oily liquid, of density 0.917, boiling at 536°. Etherole submitted to a low temperature, deposits crystals of *etherine*, which are long prisms of great lustre, fusing at 230° and boiling at 500° (260° cent.); of density 0.980. These two compounds are isomeric, and consist of carbon and hydrogen, in the same proportions as in olefiant gas.

Ethionic and isethionic acids, produced by M. Magnus, by the action of anhydrous sulphuric acid on absolute alcohol. A crystalline compound of olefiant gas and anhydrous sulphuric was obtained by M. Regnault, which may be separated by $C_4H_4+4SO_3$, or by $C_4H_4O,S_2O_5+2SO_3$, that is, as containing hyposulphuric acid united with another base, different from oxide of ethyl, with sulphuric acid. A crystalline compound was also obtained by Magnus, by exposing absolute alcohol to the vapour of anhydrous sulphuric acid, and named by him *carbyle*, which appears to be the same. Saturated with carbonate of barytes, carbyle gave free sulphuric acid and the soluble *ethionate of barytes*, which last contains the same elements as sulphovinate of barytes, indicating the assumption of the elements of an atom of water by the carbyle. *Ethionic acid* may be procured by adding dilute sulphuric acid cautiously to a solution of ethionate of barytes. It is a compound of small stability, and is decomposed by boiling like sulphovinic acid, giving alcohol and *isethionic acid*, the last of which does not undergo farther decomposition. The salts of the latter are likewise isomeric, when dried, with the sulphovinates. Isethionic acid may be concentrated, and stands 302° (150° cent.) without decomposition. All its salts are neutral to test-paper, and are also remarkably stable, supporting a temperature of 482° (250° cent.) without decomposition. When fused with an alkaline hydrate, they leave as a residue a mixture of the sulphite and sulphate of the alkali, from which it is inferred that they contain hyposulphuric acid, and not sulphuric acid.

Isethionate of barytes is prepared by passing pure olefiant gas through anhydrous sulphuric acid, in the liquid state; or by saturating ether in a flask surrounded with ice, by the same acid. The acid solution is afterwards boiled, so long as alcohol is disengaged, and then saturated with carbonate of barytes. This salt is represented by $BaO,C_4H_5O_2+S_2O_5$. *Isethionate of copper* crystallizes in regular octohedrons, of an emerald green colour, containing 2 atoms of water of crystallization, which they lose at 482° (250° cent.), and become white and opaque. From none of these salts can alcohol or ether be derived; they do not, therefore, contain ethyl.

Two other acids of this class have been obtained, *methionic acid*, by saturating ether with anhydrous sulphuric acid, without cooling the mixture, of which the salt of barytes, $BaO,C_2H_3S_2O_7$, is insoluble in alcohol; and *althionic acid*, which is found in the residue of the preparation of olefiant gas by means of alcohol and sulphuric acid, of which the salts are isomeric with the sulphovinates, although distinguishable from them by their properties (Ettling, Regnault).

The compounds which follow are derived from the oxidation of alcohol and its derivatives.

SECTION III.

ACETYL SERIES OF COMPOUNDS.

Acetyl C_4H_3=Ac: a hypothetical radical, produced by the abstraction of 2 atoms of oxygen from ethyl, by oxidating processes, and which pervades a series of compounds, including acetic acid, from which it derives its name.

The following are the oxygen compounds of acetyl.

Acetyl	C_4H_3	
Oxide of acetyl . .	C_4H_3O . .	unknown
Hydrate of oxide of acetyl	$C_4H_3O + HO$	aldehyde
Acetous acid . . .	$C_4H_3O_2 + HO$	aldehydic acid
Acetic acid . . .	$C_4H_3O_3 + HO$	acetic acid.

HYDRATE OF THE OXIDE OF ACETYL, OR ALDEHYDE.*

Formula, $C_4H_3O + HO$. It will be observed that aldehyde occupies the same place in the acetyl series that alcohol does in the ethyl series. It was obtained in an impure state by Dobereiner, and afterwards isolated, and its true nature ascertained by Liebig. Aldehyde is formed by the action of oxidating bodies upon alcohol, by which 2 atoms of hydrogen are abstracted, and the elements of aldehyde left. It is occasionally produced during the absorption by alcohol of oxygen from the air, in the process of acetification, and is a product of the action of dilute nitric acid upon alcohol, but it is usually prepared by the action of dilute sulphuric acid with peroxide of manganese upon alcohol.

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* From *alcohol dehydrogenatum*.

To prepare aldehyde, a mixture is distilled by a gentle heat of 6 parts of sulphuric acid, 4 parts of water, and 4 parts of rectified spirits of wine, and the product carefully condensed, so long as chemical action appears to take place from the frothing up of the materials in the retort. The distilled liquid, which is a mixture of aldehyde with water and several other secondary products, is distilled by a water-bath from an equal weight of chloride of calcium, till one half of it passes over. But to free the aldehyde from foreign bodies, it is necessary to unite it with ammonia; the product of the last distillation is therefore diluted with an equal volume of ether, and the mixture saturated at a low temperature with ammoniacal gas; the compound, or ammonia-aldehyde is deposited in colourless crystals, which are afterwards washed with ether and dried in air. Two parts of ammonia-aldehyde dissolved in 2 parts of water are distilled with 3 parts of sulphuric acid diluted with 4 parts of water, and the product condensed in a receiver surrounded with ice. It is afterwards rectified from chloride of calcium, by a heat not exceeding 77 or 86° (25 or 30° cent.).

Aldehyde is a colourless, highly-fluid liquid, of a peculiar ethereal and suffocating odour, boiling at 71.6° (22° cent.) of density 0.790 at 64.4° (18° cent.), neutral, and very combustible. It is miscible with water, alcohol and ether. It changes in the air into acetic acid by absorption of oxygen. It dissolves phosphorus, sulphur and iodine.

When pure and anhydrous aldehyde is kept for some time at 32°, it gradually loses its power to mix with water, and is transformed into a coherent mass, composed of long transparent needles, resembling icy spiculæ. This is *Elaldehyde*, which is similar in composition to aldehyde, but of three times the atomic weight, judging from the density of its vapour. Elaldehyde fuses at 35.6° (2° cent.), and boils at 201.2° (94° cent.).

Metaldehyde is another product of the condensation of the elements of aldehyde, which appears at the ordinary temperature in aldehyde left for some time in a well-stopped phial, in the form of white and transparent needles, or colourless prisms, which gradually attain a certain magnitude. It sublimes at 248° without fusing, and condenses in the air in snowy and very light flocks. It is insoluble in water, but dissolves easily in alcohol. The density of its vapour has not been determined.

Aldehyde is capable of combining directly with ammonia and potash, thus evincing an approach to the acid character.

Ammonia-aldehyde, C_4H_3O,NH_3+HO, crystallizes in acute rhombohedrons, which are transparent, and of great lustre. These crystals fuse between 70 and 80° cent. and distil without alteration at 100° cent.

Acetal, or compound of aldehyde with ether, $AcO,EO+HO=C_8H_9O_3$, was discovered by Dobereiner, and is formed by the action of platinum black on the vapour of alcohol with the presence of oxygen. Acetal is a colourless very fluid liquid, having a peculiar odour, suggesting that of Hungary wines. It boils at 95.2° cent., its density is 0.823 at 20° cent. It is soluble in 6 or 7 parts of water, and mixes with alcohol in all proportions.

Resin of aldehyde is a product of the decomposition of aldehyde by alkalies, with the assistance of air.

ACETOUS OR ALDEHYDIC ACID.

Formula of the hydrated acid, $C_4H_3O_2+HO=AcO_2+HO$. This acid is formed when aldehyde is heated in contact with oxide of silver, one half of the oxide being reduced to the metallic state, while the other half unites with the aldehydic acid formed. If to water in a test-tube containing a few drops of aldehyde, a little nitrate of silver be added, and ammonia so as to precipitate the oxide of silver, and then the tube be rapidly heated by the flame of a spirit-lamp, the silver is deposited on the tube with a bright surface, like a mirror, and forms a beautiful experiment. When the salts of this acid are evaporated, they become brown, and undergo decomposition.

ACETIC ACID.

Formula of the hydrated acid $HO+C_4H_3O_3=HO+AcO_3$.

Vinegar has long been derived by the action of air upon alcoholic liquors, such as wine and beer, but the remarkable discovery of Dr. J. Davy, that platinum black in contact with alcohol became incandescent, and gave rise to acetic acid, first led Dobereiner to the discovery that alcohol by absorbing oxygen, gives rise to water and acetic acid, without disengaging carbonic acid. He found that the elements of 1 atom of alcohol absorb 4 atoms of oxygen, with the formation of 1 atom of anhydrous acetic acid, and 3 atoms of water:

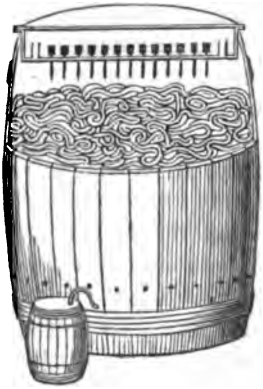
$$C_4H_6O_2 \text{ and } 4O = C_4H_3O_3 \text{ and } 3HO.$$
$$\text{or } C_4H_5O + HO \text{ and } 4O = HO,C_4H_3O_3, + 2HO.$$

Hence, when alcohol is converted into acetic acid, 2 atoms of oxygen are directly absorbed, and 2 atoms of oxygen convert 2 atoms of hydrogen into water. The atom of water of the alcohol and the 2 atoms of water produced, are all retained, and form a remarkable terhydrate of acetic acid.

Pure alcohol, diluted with water and exposed to air, does not acidify; the presence of some foreign organic matters, which exist in wine and beer, is necessary to act as a ferment, and to place the alcohol in a condition to absorb oxygen. This ferment is no doubt an oxidable azotised matter. Some kinds of beer, in which the ferment has been completely exhausted and precipitated by a preceding highly-protracted vinous fermentation, such as the Bavarian beer, are not liable to become sour or undergo the acetous fermentation. The rapid process of acidifying alcohol, introduced into Germany by MM. Wageman and Schuzenbach, is the most interesting, in a scientific point of view.

Strong alcohol is diluted with 4 or 6 parts of water, and about 1-1000th of yeast, must of beer, vinegar or honey added to it. To acidify this liquid, it is heated to 75 or 80°, and made to trickle through a cask, filled with beech-wood shavings, (Fig. 95), and pierced with holes at top and bottom to allow a circulation of air through it. From the great surface exposed by the liquid, the absorption of oxygen is most rapid, and the temperature rises to 100 or 104°. When the liquid has been passed three or four times through the barrel, at the high temperature, all the alcohol it contains is changed into vinegar; an operation which may be completed in twenty-four or thirty-six hours. The addition of certain aromatic substances, such as the essential oils, or a mere trace of wood vinegar, entirely prevents the acidification of the alcohol.

FIG. 95.



Wood vinegar, or pyroligneous acid is prepared on a large scale by the distillation of wood, generally that of oak coppice deprived of the bark, which is used in tanning. The watery fluid containing the acid, and tarry matter which distil over together, are separated, mechanically, in a great measure, by subsidence. The acid may be freed from a portion of the empyreumatic oils it holds in solution, by a single distillation. It is purified completely by neutralising it with lime, crystallizing the acetate of lime repeatedly, decomposing the latter by sulphate of soda, and fusing the acetate of soda by a high temperature, at which the empyreumatic matters are volatilised or destroyed. By distilling 3 parts of the acetate of soda, well dried and in powder, with 9.7 parts of sulphuric acid, a highly concentrated and pure acetic acid is obtained.

The proportions last mentioned give 2 parts of a hydrated acetic acid, which is distilled again, and the two last thirds of distilled liquid exposed to 24 or 25°, for the protohydrate of acetic acid, which crystallizes. The crystals may be drained, fused, and crystallized again, to obtain the hydrate of acetic acid in a state of purity. Below 63°, the hydrate crystallizes in shining transparent plates or tables, which fuse above 63° into a limpid liquid, of density 1.063; it boils at 248°. The odour of this acid is penetrating and characteristic; it forms blisters on the skin, like a mineral acid. The liquid acid mixes with water, alcohol, ether, and several essential oils in all proportions. It dissolves camphor and some resins. The vapour of the acid in a state of ebullition may be kindled, and burns with a pale blue flame, producing water and carbonic acid. Nitric acid has no action on acetic acid; sulphuric acid with heat blackens acetic acid, with an evolution of sulphurous acid.

Acetic acid increases somewhat in density by a slight dilution; the greatest condensation occurring in the hydrate consisting of 1 atom of anhydrous acid and 3 atoms of water, of which the density is 1.07. The strength of a dilute acetic acid is best ascertained by the quantity of marble it dissolves.

Acetic acid forms neutral salts, and with many metallic oxides sub-salts containing 2 and 3 atoms of base to 1 atom of acid. Most of its neutral salts are soluble. It is recognised in combination by the peculiar odour of acetic acid evolved when concentrated sulphuric acid is added. M. Liebig recommends as the most certain means of discovering the presence of acetic acid, or of an acetate in any substance, to distil it with dilute sulphuric acid, and to place the product in contact with oxide of lead in the cold. If there is any acetic acid present, the oxide of lead dissolves, and the solution exhibits an alkaline reaction. (Traité, i. 398).

Acetate of oxide of ethyl, acetic ether, $C_4H_5O+C_4H_3O_3=EO,\bar{A}$. Alcohol is only decomposed to a small extent when distilled with strong acetic acid. The ether is prepared by distilling, with a heat moderate at first, but afterwards increased, 4.5 parts of strong alcohol and 6 parts of concentrated sulphuric acid, previously mixed and cooled, with 16 parts of anhydrous acetate of lead. The product is neutralised with a little lime, then poured over an equal bulk of chloride of calcium in a tubulated retort, and distilled again by a water-bath. Acetic ether is a liquid of an agreeable refreshing odour, and is the source of the refreshing odour of some kinds of vinegar which contain it. Its density is 0.89 at 59°; it boils at 165.2° (74° centig.). Acetic ether is soluble in 7 parts of water, and in alcohol and ether in all proportions. It is decomposed by alkalies with the greatest facility.

Acetic acid forms neutral and bisalts with the alkalies. The neutral solution of *acetate of ammonia*, the spirits of mindererus, is used in medicine. *Acetate of potash* is a foliated crystalline mass, anhydrous, and slightly deliquescent. *Acetate of soda* crystallizes with 6 atoms of water; it is soluble in three times its weight of cold water, and in five times its weight of alcohol. Its taste is saline, cooling and agreeable. *Acetate of barytes* crystallizes below 59° with 3 atoms of water, and is isomorphous with acetate of lead; at a higher temperature it crystallizes with 1 atom of water. It is very soluble in water, and more so at a low than at a high temperature. *Acetate of strontian* crystallized below 59° (15° cent.) contains 4 atoms of water, and crystallized above that temperature only half an equivalent of water. *Acetate of lime* crystallizes with water. A concentrated and boiling solution of it treated with sulphate of soda, in the preparation of acetate of soda, allows a double *sulphate of lime and soda* to precipitate. *Acetate of magnesia* is very soluble, and crystallizes with difficulty.

Acetate of alumina is obtained in solution, when acetate of lead barytes or lime is precipitated by sulphate of alumina, and is much used in dyeing. This salt is decomposed in drying, or by a slight heat, into free acetic acid and a subacetate of alumina which is insoluble. The solution of the pure salt may be boiled without decomposition, but if sulphate of potash, or any other neutral salt of an alkali be present, the solution becomes turbid when heated, and a basic salt precipitates, which dissolves again on cooling (Gay-Lussac). *Acetate of manganese* is used in dyeing, and is prepared for that purpose by mixing acetate of lime with sulphate of manganese. This salt is crystallizable. *Acetate of zinc* crystallizes with 3 atoms of water. *Acetates of iron*: a mixture of the acetates of protoxide and peroxide of iron, employed as a mordant for dyeing black, is prepared directly by dissolving old iron hoops, &c. in crude wood vinegar, with access of air. The *acetates of lead* have already been described (page 594); also the *acetates of copper* (page 584), acetate of black oxide of mercury (page 653), and acetate of silver (page 673).

SECTION IV.

PRODUCTS OF THE ACTION OF CHLORINE, BROMINE, AND IODINE UPON ETHYL, ACETYL, AND THEIR COMPOUNDS.

Oxichloride of ethyl, $C_4H_3Cl_2O$,(1), is an oily colourless liquid, obtained by saturating anhydrous ether with dry gaseous chlorine, cooling the mixture at the beginning, and heating it towards the end of the operation. As in the formation of acetic acid, 2 atoms of hydrogen are oxidated and withdrawn by the action of the oxygen of the air upon alcohol, and replaced by 2 atoms of oxygen, so in the action of chlorine upon alcohol, a similar change occurs, of which the product is the oxichloride of acetyl. When heated with potassium, this compound gives chloride of potassium, and a gaseous body, containing only half the chlorine in the original substance, or C_4H_3ClO, (2), observed by Malaguti. By the action of chlorine upon the vapour of pure ether in sun-shine Regnault obtained another crystalline compound C_4Cl_5O, (3), in which the whole hydrogen of ether is replaced by chlorine. Felix d'Arcet has also observed an accessory product in the preparation of Dutch liquid, which had the composition C_4H_4ClO, (4). It is named *chloretheral* by him. It will be observed that the fourth, first and third of these bodies are compounds, in which 1, 2 and 5 atoms of the hydrogen of chloride of ethyl are replaced by chlorine, without any other change of composition. They are all neutral bodies.

Oxisulphuret of acetyl, $C_4H_3S_2O$; a compound in which 2 atoms of the hydrogen of oxide of ethyl are replaced by 2 atoms of sulphur, is obtained by the action of sulphuretted hydrogen upon the oxichloride of acetyl. Another compound is formed at the same time, in which 1 atom of chlorine remains, and only 1 atom of sulphur is introduced, C_4H_3ClSO.

Acetate of oxichloride of acetyl, $C_4H_3Cl_2O+\bar{A}$, a body formed by the action of chlorine upon acetic ether, in which 2 atoms of the hydrogen of the ether are replaced by 2 atoms of chlorine; or the oxichloride of acetyl is formed, and continues in combination with the acetic acid. The benzoate of oxide of ethyl gives a compound, of which the formula is $BzCl+C_4H_3Cl_2O$.

Chloroxalic ether, $C_6Cl_5O_4$ or $C_4Cl_5O+C_2O_3$; formed by the action of chlorine on oxalic ether, crystallizable, fusible at 291°, not volatile. *Cloroxamethane*, $C_6Cl_5O_4+C_2O_2,NH_2$; formed by the action of ammoniacal gas on the ether, crystallizable, fuses at 273°, boils above 392°, volatile. *Chloroxalovinic acid* is obtained by the action of solution of ammonia upon chloroxamethane (Malaguti, An. de Chim. lxxiv, 299).

Chloride of acetyl, &c.—The following table exhibits the composition and some of the properties of the series of compounds formed by Regnault, by treating the chloride of ethyl and the products thus obtained, successively with chlorine (An. de Ch. lxxi, 353):

	Spec. grav.	Boiling point.	Density of vapour.	
$C_4H_5Cl_1$	0.874*	11° centig.	2219	4 vol.
$C_4H_4Cl_2$	1.174	64° ..	3478	..
$C_4H_3Cl_3$	1.372	75° ..	4530	..
$C_4H_2Cl_4$	1.530	102° ..	5799	..
$C_4H_1Cl_5$	1.644	146° ..	6975	..

* At 11° cent.; the others between 18 and 20° cent.

CHLORAL.

Formula: $C_4HCl_3O_2=C_4Cl_3O+HO$.

This singular liquid, of which we owe the discovery to Liebig, may be considered as the hydrate of oxide of acetyl (aldehyde), in which the whole hydrogen of the acetyl is replaced by chlorine:

Hydrate of oxide of acetyl . . .	C_4H_3O+HO.
Chloral	C_4Cl_3O+HO.

It cannot, however, be prepared directly by the action of chlorine upon aldehyde, owing to the facility with which the latter body changes, but it is the ultimate product of the action of chlorine upon anhydrous alcohol. It is recommended in preparing chloral, to introduce a few ounces of perfectly anhydrous alcohol into the body of a tubulated retort, supported with its beak somewhat elevated, and with a glass tube adapted by a cork to the mouth, and directed upwards, so that what condenses may flow back into the body of the retort. Chlorine gas carefully dried by being passed through sulphuric acid, which is renewed from time to time during the process, is conducted by a tube entering the tubulure of the retort, and made to stream through the alcohol, the body of the retort being immersed in cold water to keep it cool at the beginning, but afterwards heated to assist in expelling the hydrochloric acid formed, towards the end of the process. An immense quantity of chlorine is required, and the gas may continue to be absorbed by a few ounces of alcohol for twelve or fifteen hours. The operation is complete when the chlorine traverses the boiling liquid without any disengagement of hydrochloric acid; a dense oleaginous liquid, the hydrate of chloral, is obtained, which often becomes a solid mass on cooling. The mass is fused by a gentle heat, and mixed in a well-stopt bottle, with two or three times its bulk of oil of vitriol, and the mixture gently heated by a water-bath; the impure chloral comes to the surface of the liquid, in the form of a limpid oil. It is drawn off, and boiled for some time to expel free hydrochloric acid and alcohol, and then distilled from an equal bulk of sulphuric acid, to deprive it of adhering water. The last product is pure chloral, except a little hydrochloric acid, which is separated by distilling again from quicklime slaked and recently ignited, discontinuing the distillation when the lime in the retort is no longer covered by the liquid; the product obtained is chloral, perfectly pure. (Liebig).

Chloral is a pretty fluid oleaginous liquid, colourless, greasy to the touch, having a penetrating disagreeable odour which provokes tears; its taste is first oily and then caustic. Its density is 1.502 at 64.4° (18° cent.), and it boils at 201.2° (94° cent.) distilling without alteration; the density of its vapour is very nearly 5000, and its combining measure, 4 volumes (Dumas). Chloral is miscible with alcohol and ether; it dissolves, apparently without alteration, sulphur, phosphorus and iodine, with the aid of heat.

Hydrate of chloral.—Chloral is first obtained from alcohol in the state of a hydrate, the water being derived from a reaction of the nascent hydrochloric acid and alcohol, which gives rise to water and chloride of ethyl. When pure chloral is brought in contact with a small quantity of water, combination takes place immediately on mixing the liquids, with evolution of heat, and in a few seconds the compound is deposited as a crystalline mass, composed of needles, which re-dissolve in a larger quantity of water. By evaporation of the solution in vacuo, the compound is obtained in large rhombohedral crystals, which contain 2 atoms of water. The solution of the hydrate of chloral is neutral, and has no action on red oxide of mercury; the dry hydrate may be distilled without change.

Insoluble chloral.—Like aldehyde pure chloral cannot be kept long without alteration. It gradually passes into a solid mass resembling porcelain, without change of weight, and equally whether contained in vessels which are hermetically sealed or open. This mass is not dissolved by water, but when placed in contact with a very small quantity of water, it slowly changes into the crystalline hydrated chloral, which dissolves at once when a large quantity of water is added to it. Insoluble chloral is modified by contact with sulphuric acid, and somewhat altered in composition; when washed with water it loses a little hydrochloric acid, and acquires some water. The formula assigned to *modified insoluble chloral* is $C_{12} H_4 Cl_8 O_7$: which is 3 atoms of chloral, minus 1 atom of hydrochloric acid plus 2 atoms of water.

Sulphuret of ether with chlorine.—Regnault has observed that the sulphuret of ethyl is powerfully acted upon by chlorine, with the assistance of light; 4 atoms of hydrogen are replaced by 4 atoms of chlorine, and the compound $C_4\ Cl_4\ HS$ formed, which is a fetid liquid, boiling about 320° (160° cent.); of density 1.673 at 75.2° (24° cent.)

Chloracetic acid, $C_4\ Cl_3\ O_3 + HO$.—This remarkable acid, in which the 3 atoms of the hydrogen of acetic acid are replaced by 3 atoms of chlorine, was obtained, by M. Dumas, by the action of chlorine gas contained in large balloons upon the hydrate of acetic acid, exposed to the direct rays of the sun for a whole day. It crystallizes in rhomboidal plates or colourless needles, which deliquesce rapidly in damp air. Chloracetic acid whitens the tongue; its vapour is suffocating and painful to the organs of respiration. It reddens litmus, without bleaching it. The crystals fuse at 45 or 46° cent.; and fused they enter into ebullition between 195 and 200° cent. The density of the fused acid at 46° cent. is 1.617. It forms a class of salts which greatly resemble the acetates; they are all soluble, and are blackened by an excess of alkali even more readily than the acetates.

Chloracetic acid exhibits a beautiful transformation when heated in contact with an alkali; it is decomposed into perchloride of formyle, a metallic chloride, and alkaline carbonate and formiate. Acetic acid gives in the same circumstances light carburetted hydrogen ($C_2\ H_4$) and an alkaline carbonate. (Dumas, An. de Ch. lxxiii, 77 and 89).

Heavy chlorinated ether. — The body which principally is formed when alcohol of 80 per cent. (0.848) is saturated with humid chlorine gas. It precipitates from the acid liquid when water is added. It is colourless, neutral, of density 1.277, and boils between 112 and 125° cent. The results of its analysis are discordant, which M. Regnault supposes to arise from intermediate chlorinated bodies, which form between aldehyde and chloral:

Aldehyde. . .	$C_4\ H_4\ O_2$
Intermediate bods.	$C_4\ H_3\ Cl\ O_2$
	$C_4\ H_2\ Cl_2\ O_2$
Chloral. . .	$C_4\ H\ Cl_3\ O_2$

Bromal, $C_4\ Br_3\ O + HO$.—This compound, which corresponds with chloral, was formed by M. Lœwig by adding 13.8 parts of bromine to 1 part of alcohol cooled by ice, adding the former in small portions, taking care that the part previously added had first disappeared. It is purified in the same manner as chloral. Bromal is a colourless oily liquid of a peculiar and very strong odour which provokes tears, and of a caustic taste. Its density is 3.34, and boiling point below 212°. Bromal is miscible with water, alcohol and ether. Caustic alkalies transform it into an alkaline formiate and perbromide of formyl. Its solution affords by evaporation a crystalline hydrate, containing 4 atoms of water, consequently 2 atoms more than the hydrate of chloral.

Brominated ether.—Lœwig has observed, that bromine in acting upon ether, produces a body analogous to heavy chlorinated ether, but respecting the composition of which there is the same uncertainty.

Iodal.—An oleaginous liquid which corresponded in some properties with chloral, was obtained by M. Aimé, by the action of 4 parts of alcohol, one part of iodine, and one part of fuming nitric acid, left in contact in a bottle imperfectly closed; but its composition was not ascertained. Mr. Johnston had previously obtained some peculiar substances by a similar reaction.

Chloride of cyanogen upon alcohol.—A slightly volatile crystalline matter is produced, when a mixture of alcohol and very concentrated hydrocyanic acid, or a mixture of alcohol and a metallic cyanide soluble in alcohol, is saturated with dry chlorine. This crystalline substance has a silky lustre, and considerably resembles sulphate of quinine. It fuses at 248°, subliming in part. Its empyrical formula is $C_{16}\ H_{14}\ O_8\ Cl_2\ N_2$, corresponding with 3 atoms of aldehyde $3(C_4\ H_4\ O_2)$, 2 atoms of chlorine Cl_2, 2 atoms of cyanogen $N_2\ C_4$, and 2 atoms of water $H_2\ O_2$. (Stenhouse).

SECTION V.

CONGENERS OF ALCOHOL OF AN UNCERTAIN CONSTITUTION.

Hydruret of acetyl, olefiant gas, etherine, elayl (Berzelius); $C_4\ H_4 = C_4\ H_3$, H or AcH.—This gas is generally prepared by heating a mixture of 1 part of alcohol with 6 or 7 parts of concentrated sulphuric acid (page 426); and is accompanied by sulphurous acid, the vapour of ether, the double sulphate of oxide of ethyl and etherole (page 772), from all of which it is purified by passing it first through milk of lime, and then through oil of vitriol. M. Mitscherlich finds it to be formed almost exclusively, when alcohol is brought into contact with oil of vitriol heated to 320° (page 772).

Pure hydruret of acetyl has a feeble ethereal odour; it is only very slightly soluble in water, oil of vitriol, alcohol and ether. It forms a crystalline compound with anhydrous sulphuric acid, $C_4\ H_4+4SO_3$. It combines with chlorine gas in equal volumes, and forms an oily liquid (a property from which it received the name of olefiant gas), the chlorhydrate (hydrochlorate) of the chloride of acetyl, known as Dutch-liquid, or the oil of olefiant gas.

Chlorhydrate of chloride of acetyl, $C_4\ H_3\ Cl,\ H\ Cl$, or $Ac\ Cl,\ H\ Cl$.—Is purified by mixing with water and distilling the product last mentioned, by a water bath; depriving it afterwards of the water which it takes up by shaking it in a bottle with sulphuric acid, and distilling again by a water bath. It is a very fluid colourless liquid, of an agreeable ethereal odour and sweetish taste; boils at 82.4° cent.; density of its vapour 3448.4. It communicates its odour to water without dissolving sensibly in it, but is soluble in all proportions in alcohol and ether. This compound may be distilled from hydrate of potash without change, but is gradually decomposed by an alcoholic solution of potash into chloride of potassium and chloride of acetyl; when this compound is heated with potassium, hydrogen gas and the chloride of acetyl are disengaged.

Chlorhydrate of chloride of acetyl readily absorbs chlorine, and by the continued action of that body a product is obtained, which by distillation furnishes two new compounds, one at 235° (115° cent.) $C_4\ H_2\ Cl_2,\ HCl$; and another at 275° (135° cent.) $C_4\ H_2\ Cl_4$. The last compound by the continued action of chlorine in diffuse day-light, or more rapidly when exposed to the direct rays of the sun, is converted into the crystalline prochloride of carbon, $C_4\ Cl_6$ (page 377).

Chloride of acetyl, $C_4\ H_3\ Cl$, = $Ac\ Cl$, separates from the alcoholic solution above referred to, in the form of gas, by the effect of a gentle heat; the gas is purified from adhering vapours of alcohol and water, by passing it through sulphuric acid. This gas has an odour which suggests that of garlic; its density is 2166, and combining measure 4 volumes. It is condensed into a limpid liquid at —0.6° (—17° cent.)

Chloride of acetyl is absorbed by perchloride of antimony ($Sb\ Cl_5$), and when the saturated solution is diluted with water, an ethereal liquid separates, consisting of a mixture of chloride of acetyl and hydrochloric acid, with a new compound $C_4H_3Cl_3$, or $C_4\ H_2\ Cl_2 + H\ Cl$. This last when distilled with an alcoholic solution of potash is resolved into chloride of potassium, water and another new volatile liquid, $C_4\ H_2\ Cl_2$, or $C_2H\ Cl$. Lastly, by continuing the action of chlorine upon the preceding bodies, the compound $C_4\ H_2\ Cl_4$ is obtained, or rather $C_4\ H\ Cl_3 + H\ Cl$, for potash transforms it into $C_4\ H\ Cl_3$, and chloride of potassium. (Regnault).

Bromhydrate of bromide of acetyl, $C_4\ H_3\ Br + H\ Br$, is a colourless liquid, boiling at 129.5° cent., obtained by passing olefiant gas into bromine.

Bromide of acetyl, $C_4\ H_3\ Br = Ac\ Br$, a gaseous body of density 3691, of which the preparation is the same as that of chloride of acetyl.

Iodhydrate of iodide of acetyl, $C_4\ H_3\ I + H\ I$.—This compound is slowly produced when iodine is left in a bottle of olefiant gas at the ordinary temperature, and sublimes in white crystals; but it is best prepared, according to Regnault, by heating iodine to 122 or 140° in a convenient vessel, and introducing pure olefiant gas into it, till all the iodine is converted into a pulverulent yellow or white substance. The compound fuses at 172.4° (78° cent.), and may be sublimed in olefiant gas, but not in air without decomposition. When heated with hydrate of potash and alcohol, there is a disengagement of olefiant gas and formation of iodide of potassium, and other products which have not been studied. This body does not furnish products corresponding with those derived from the chlorhydrate of the chloride of acetyl, when decomposed; it is very doubtful, therefore, whether the former is similar in constitution to the latter, as represented above.

Chloroplatinate of chloride of acetyl, $C_4H_3PtCl_2 = C_4H_3Cl +$

PtCl, or AcCl + Pt Cl.—This compound is formed by the action of bichloride of platinum upon alcohol, together with aldehyde, but it is best prepared from a double compound, which it forms with chloride of potassium or chloride of ammonium. Pure bichloride of platinum containing no free nitric acid is dissolved in alcohol; a small quantity of free hydrochloric acid, and a quantity of chloride of potassium equal to one eighth of the weight of the bichloride of platinum are added to this solution, and the whole digested for several hours at the temperature of boiling water. The excess of alcohol is removed by distillation, and the residue saturated with carbonate of potash. By evaporating at a gentle heat the compound in question is obtained in the crystalline form, and may be purified by new crystallizations. (Liebig's Traité). By dissolving this compound in a little water and adding bichloride platinum to the solution, so long as the double chloride of platinum and potassium precipitates, a yellow liquid is obtained, which ought to be evaporated in a dry vacuum in the absence of light. There results a gummy mass of a honey yellow colour, liable to be blackened by light, which is the chloroplatinate of the chloride of acetyl. It dissolves slowly in water and alcohol; these solutions have an acid reaction. The hydrochloric acid of Dutch-liquid being represented by proto-chloride of platinum, Pt Cl, the compound described and Dutch-liquid may be considered as analogous:

Chlorhydrate of chloride of acetyl. . .	Ac Cl + H Cl.
Chloroplatinate of chloride of acetyl. .	Ac Cl + Pt Cl.

But various other views of the constitution of this compound have been proposed.

Chloroplatinate of chloride of acetyl and potassium, Ac Cl, Pt Cl + K Cl.—The discovery of this salt, of which the preparation has just been described, is due to Berzelius. It crystallizes in semi-transparent regular prisms, of a lemon yellow colour, which abandon 4.625 per cent of water of crystallization at 212° and become quite opaque. It is soluble in alcohol, and also in 5 parts of hot water, and is less soluble in cold water. The solution is partially decomposed when heated to 194°, metallic platinum being precipitated and hydrochloric acid liberated, which last protects the salt from further decomposition.

Chloride of ammonium and chloride of sodium form corresponding double salts with the chloroplatinate of chloride of ethyl.

Ammoniacal chloroplatinate of chloride of acetyl.—Ammonia or the carbonate of ammonia throws down a lemon yellow precipitate from the solution of these double compounds, in which the chloroplatinate of chloride of acetyl is united with the elements of one atom of ammonia: $Ac\ Pt\ Cl_2 + NH_3$. It is soluble in alcohol; sparingly soluble in cold water; and its solution cannot be evaporated without decomposition.

SECTION VI.

PRODUCTS OF THE ACTION OF HEAT UPON THE ACETIC ACID OF THE ACETATES.

ACETONE.

Syn. *Pyroacetic spirit, mesitic alcohol, bihydrate of mesitylene* (*Kane*). Empyrical formula $C_3\ H_3\ O$.

The vapour of strong acetic acid passed through a porcelain tube heated to dull redness is decomposed without the deposition of any charcoal, being converted entirely into the vapour of acetone, which condenses, and a mixture of gases, containing carbonic oxide, carbonic acid and carburetted hydrogen. If the temperature exceeds a dull red heat, the products are a brown empyreumatic oil, inflammable gases and a deposit of charcoal. Anhydrous acetic acid contains the elements of 1 atom of carbonic acid and 1 atom of acetone:

$$C_4\ H_3\ O_3 = CO_2 \text{ and } C_3\ H_3\ O.$$

The acetates of the stronger bases which retain carbonic acid at a red heat, when submitted to destructive distillation become carbonates, and supply no volatile product except acetone. The acetates of earths of which the carbonates are decomposed at a red heat, such as magnesia, afford a mixture of acetone and carbonic acid, when distilled; and acetates of bases which are easily reduced, such as the acetates of copper and silver, yield hydrated acetic acid, carbonic oxide, carbonic acid, water and acetone, the residuum containing a mixture of the metal and highly divided charcoal. Acetone also appears among the products of the distillation with an alkali of sugar and other ternary compounds of carbon, oxygen and hydrogen (page 710).

Acetone may be conveniently prepared by distilling a mixture of 2 parts of crystallized acetate of lead and 1 part of quick-lime in a salt-glaze jar (greybeard), the lower part of the jar being coated with fire-clay, and a bent glass tube half an inch in diameter adapted to the mouth by a cork, so as to form a distillatory apparatus. The jar is supported in the mouth of a small furnace, by which the lower part of the jar only is heated to redness, and the vapours conducted into a Liebig's condenser. The product is redistilled from quick lime repeatedly, till its boiling point is constant at 132°.

Acetone is a limpid colourless liquid, having a peculiar penetrating and slightly empyreumatic odour. Its density in the liquid state is almost the same as that of alcohol 0.7921, and the density of its vapour 2022, air being 1000; its taste is disagreeable and analogous to that of peppermint. It is miscible in all proportions with water, alcohol and ether. Many salts which are soluble in alcohol and water are insoluble in acetone, particularly chloride of calcium and hydrate of potash; acetone is separated from water, by dissolving such salts in the mixture of these liquids. Acetone is highly inflammable and burns with a white flame.

On rectifying acetone derived from the acetates, a less volatile oleaginous body remains in the retort, which has been examined by Dr. Kane and named *dumasine*. This empyreumatic oil has a disagreeable odour and burning taste; it boils at 248° (120° cent.); its composition is expressed by $C_{10} H_8 O$; the density of its vapour is 5204, and its combining measure 4 volumes.

Metacetone, $C_6 H_5 O$, which is also obtainable from sugar, has already been described.

Dr. Kane who examined acetone and the products of its decomposition several years ago, then assigned to the former the constitution of an alcohol, doubling its atomic weight and giving it the formula:

$$C_6\,H_5\,O+HO.$$

The bodies derived from it, which I can only notice very shortly, were named by him on that theory.

Mesitylene, $C_6\,H_4$.—This hydrocarbon is an oily colourless liquid, obtained on distilling acetone with half its volume of fuming sulphuric acid. It is obviously formed by the abstraction of the elements of 2 atoms of water from acetone. Sulphuric acid, nitric acid and chlorine react upon mesitylene in the same way as they do upon benzin (benzole). Mesitylene is lighter than water; it boils at 276.4° (135.5° cent.) Later in the distillation of the materials which yield that oil, another oil which resembles it much passes over, but of which the boiling point is more elevated. The formula of the second oil appears to be $C_6\,H_3$.

Oxide of mesityle, $C_6\,H_5\,O$ (Kane).—Is obtained on adding caustic potash to the chloride of mesityle; a limpid colourless liquid, not miscible with water, having the odour of peppermint; it boils at 248°.

Chloride of mesityle, $C_6\,H_5\,Cl$ (Kane).—Produced by the direct action of hydrochloric acid upon acetone, or by adding 2 parts of perchloride of phosphorus gradually to 1 part of acetone. An oily liquid denser than water, and not miscible with that liquid.

Chloroplatinate of oxide of mesityle, $C_6\,H_5\,O$, $Pt\,Cl_2$ (Zeise); named *metacechlorplatin* by Zeise.—Obtained by distilling a solution of 1 proportion of bichloride of platinum with 2½ proportions of acetone, when hydrochloric acid and an ethereal body pass over into the receiver, and a brown acid residue is left in the retort. The residue contains a resinous matter which Zeise names the *resin of platinum*; the aqueous solution derived from washing the resin, becomes turbid after a time, and deposits the compound in question in small yellow crystals which lose nothing at 212°. It is slightly soluble in water; the solution is decomposed by ebullition. When the mother liquor of these crystals is distilled, there is a disengagement of gas, and a black flocculent powder is precipitated, which is explosive by heat. Zeise has named it *pyracechlorplatin.*

Sulphomesitilic acid.—By the action of fuming sulphuric acid upon acetone there is produced among other products, an acid of which the salt of lime is expressed by:

$$CaO,\ C_3\ H_3\ O+SO_3.$$

This salt loses the elements of half an atom of water by heat. Its acid does not correspond with sulphovinic acid as the saturating power of the sulphuric acid in the former is not injured by the acetone, while it is diminished one half by the oxide of ethyl in the latter. Nor can acetone be reproduced from sulpho-mesitylic acid by any means. Acetone likewise affords no peculiar acid by its oxidation, as alcohol does acetic acid. Hence acetone is deficient in what are now considered the three most essential characters of an alcohol.

When 2 measures of acetone are mixed with 1 measure of hydrate of sulphuric acid, and the liquid diluted with water and neutralised with lime, a new salt is obtained analogous to the former, but containing twice as much acetone:

$$Ca\ O,\ C_6\ H_6\ O_2+SO_3.$$

The acid of these salts undergoes decomposition when deprived of its base by sulphuric acid, and evaporated.

By the action of nitric acid upon acetone Dr. Kane obtained the two following bodies, the composition of which, however, is somewhat doubtful:

Nitrite of oxide of pteleyl. . . . $C_3\ H_3\ O+NO_3$;
Mesitic aldehyde. . . . . $C_3\ H_3\ O_2$.

By the action of phosphoric acid and of phosphorus with iodine, two acids were also obtained: *phosphomesitylic acid* and *hyphosphomesitylous acid,* the formula of the salt of barytes of the latter being, $Ba\ O,\ C_6\ H_6\ O_3\ P$.

Mesitic chloral, $C_6\ H_4\ Cl_2\ O_2$ (Dumas, Kane).—Obtained by passing dry chlorine through acetone, till the disengagement of hydrochloric acid ceases. It is a liquid of a penetrating insupportable odour, insoluble in water; density 1.33, and boiling point 258.8° (126° centig.)

Chloride of pteleyl, $C_3\,H_3\,Cl$ (Kane).—A crystalline substance obtained by passing a current of chlorine into mesitylene.

SECTION VII.

ARSENICAL COMPOUNDS DERIVED FROM ACETYL.

By the dry distillation of equal weights of acetate of potash and arsenious acid, a remarkable liquid is obtained known as the *liquor of Cadet* or *alcarsin.* This liquid may be supposed to be formed by the abstraction of 2 atoms of carbonic acid from the elements of 2 atoms of acetone and 1 atom of arsenious acid:

2	atoms	acetone.	$C_6\,H_6\,O_2$
1	„	arsenious acid.	$As\,O_3$
—2	„	carbonic acid.	$C_2\,O_4$
1	„	alcarsin.	$C_4\,H_6\,As\,O$

This is a body remarkable for its insupportable odour and spontaneous inflammability in air. The mode of formation and oxidability of alcarsin, favour the idea that it belongs to the acetyl series and contains arseniețted hydrogen. In the following scheme of the composition of alcarsin and its derivatives, the former is represented as containing the hypothetical oxide of acetyl and arseniețted hydrogen (Liebig):

Alcarsin.	$Ac\,O + As\,H_3$
Chlorarsin.	$Ac\,Cl + As\,H_3$
Sulpharsin.	$Ac\,S + As\,H_3$
Cyanarsin.	$Ac\,Cy + As\,H_3$
Alcargen.	$Ac\,O_3 + As\,H_3 + HO$

Berzelius, however, considering the pre-existence of arseniețed hydrogen in these compounds as improbable, presumed alcarsin to be the oxide of a compound radical, which he named *cacodyl* (from κακος and ὀδυς), in reference to the repulsive odour of alcarsin. The same theory is adopted by M. Bunsen, who has devoted great labour and much ingenuity to the painful investigation of this class of bodies, of which the sensible properties are most offensive and dangerous. M. Bunsen has succeeded also in isolating cacodyl, the supposed radical of the series, a discovery of much interest for the theory of compound radicals.

CACODYL.

Formula $C_4\ H_6\ As = Kd$.

Cacodyl is a liquid obtained from the continued digestion of the chloride of cacodyl with metallic zinc at 230°, and dissolving out the chloride of zinc formed by water. It is dried by quicklime, distilled in a glass retort filled with carbonic acid to exclude air and crystallized repeatedly at 21.2° (—6° centig.)

Cacodyl is an ethereal limpid liquid (greatly resembling its oxide), of a nauseous odour, which crystallizes in shining prisms at 23°. It takes fire spontaneously in air and in chlorine gas, with the formation of a cloud of white smoke. It sinks in water, in which liquid it is insoluble; it is soluble in alcohol and ether. Its boiling point is about 338° (170° cent.); the density of its vapour by experiment 7101, by theory 7281; its combining measure 2 volumes. Its vapour is decomposed at a red heat into arsenic, olefiant gas and light carburetted hydrogen.

Oxide of cacodyl, alcarsin, $C_4\ H_6\ As + O = Kd\ O$.—Is prepared by the distillation of a mixture of equal weights of dry acetate of potash and arsenious acid. At the same time metallic arsenic distils over, with acetic acid and acetone which float in the receiver above the fluid alcarsin. The latter is obtained pure by washing with water free from air, and by distillation from quicklime in a retort filled with hydrogen gas, and from which atmospheric air is most carefully excluded. Oxide of cacodyl is also produced by the direct oxidation of cacodyl from slow access of air; and also from the partial reduction of cacodylic acid by phosphorous acid.

Oxide of cacodyl is an ethereal limpid liquid, of very considerable refracting power, 1.762; it boils at about 302° (150° cent.), and solidifies in the form of white silky plates at —9.4° (—23° cent.) Its odour suggests that of arsenietted hydrogen, is most disgusting, and provokes a copious flow of tears. The density of its vapour is 7555 by experiment, and 7833 by theory; its combining measure 2 volumes. It takes fire spontaneously in air and burns with a white flame and strong odour. Taken internally alcarsin is a violent poison.

Oxide of cacodyl is but slightly soluble in water, but dissolves in all proportions in alcohol and ether. It dissolves in caustic potash colouring the latter brown; dilute nitric acid dissolves it without disengagement of gas, but when heated decomposition occurs. Oxide of cacodyl dissolves phosphorus, sulphur and iodine; the solution of the last is colourless and deposits crystals, which disappear again when an excess of iodine is added. It combines with the hydrate of sulphuric acid, forming thin needles which have an acid reaction and are deliquescent. Besides combining with acids, oxide of cacodyl combines also with salts. When its solution in alcohol is mixed with a solution of chloride of mercury, a white precipitate falls, soluble in hot water and crystallizing from it, which is a compound of 1 atom oxide of cacodyl, and 2 atoms chloride of mercury. This compound is inodorous. It yields with hydrochloric acid, chloride of mercury and chloride of cacodyl. Oxide of cacodyl forms a similar compound with bromide of mercury. It reduces the salts of the suboxide and oxide of mercury.

Cacodylic acid, alcargen, $HO, C_4 H_6 As O_3 = HO + Kd O_3$.—Cacodyl and its oxide left under water to the slow action of air, oxidate so as to become cacodylic acid. The hydrated acid crystallizes in large colourless prisms, is inodorous, not poisonous, fusible, soluble in water and in alcohol. It is reduced to the state of chloride of cacodyl by chloride of zinc, and to the state of oxide of cacodyl by phosphorus acid. Alcargen has a feeble acid reaction; it combines with the alkalies, giving rise to compounds which have the aspect of gum and are not obtained under regular forms. It dissolves in the hydrate of sulphuric acid without being modified; is not attacked by anhydrous sulphuric acid, and is oxidated with difficulty by nitric acid and aqua regia.

M. Bunsen adds one atom of oxygen to the formula for alcargen, but Liebig has shewn that the formula as given above is more in accordance with Bunsen's analysis of alcargen than his own view.

Sulphuret of cacodyl, $C_4 H_6 As + S = Kd S$, may be obtained directly by uniting cacodyl with 1 atom of sulphur, or by the distillation of chloride of cacodyl with sulphuret of potassium.

This body is also a product of the decomposition of oxide of cacodyl by sulphuretted hydrogen gas. It is an ethereal liquid, of a highly disagreeable smell, which does not fume in air, is heavier than water and insoluble in that liquid. The density of its vapour is by experiment 7810, by calculation 8390, its combining measure 2 volumes. It is resolved by hydrochloric acid, into sulphuretted hydrogen and chloride of cacodyl.

Persulphuret of cacodyl of the composition $2C_4H_6As + 5S = 2\ Kd + 5S$, is formed when sulphur is dissolved in the preceding compound or in cacodyl itself. It may be crystallized from ether in colourless prisms, which fuse at 109.4° (43° cent.) A *protoseleniuret of cacodyl* has also been formed.

Chloride of cacodyl, $C_4\ H_6\ As + Cl = Cd + Cl$, is formed by the digestion of oxide of cacodyl in hydrochloric acid, or by the slow action of chlorine on cacodyl. It is a colourless ethereal liquid, which does not fume in air, does not solidify at —49° (—45° cent.), and is converted a little above 212° into a colourless vapour, which inflames in the air. Its odour is extremely penetrating and stupifying. The density of its vapour is by experiment 4560, by calculation 4860; its combining measure 2 volumes. Chloride of cacodyl combines with metallic chlorides.

Similar compounds of cacodyl with *bromine*, *iodine*, and *fluorine* have been formed.

Oxichloride of cacodyl, $Kd\ O + 3\ Kd\ Cl$, is formed by treating the chloride with water, or by distilling it with hydrochloric acid. The density of its vapour is by experiment 5460, by calculation 5300; its combining measure 3 volumes. It is a liquid very like the oxide, boiling at 228.2° (109° cent.) A corresponding *oxibromide of cacodyl* and an *oxyiodide of cacodyl* have been formed.

Cyanide of cacodyl, $C_4\ H_6\ As + N\ C_2 = Kd\ Cy$, is produced by the distillation of concentrated hydrocyanic acid or of a solution of cyanide of mercury with oxide of cacodyl. It crystallizes in fine prisms of a diamond lustre, highly limpid, which emit a strong and insupportable odour. It is insoluble in water, fusible at 91.4° (33° cent.) and crystallizable by cooling. Its density in the state of vapour is 4650 by experiment, and 4540 by calculation; its combining measure 2 volumes. The cyanide is the most poisonous of the compounds of cacodyl.

It will be observed that oxide of cacodyl or alcarsin corresponds in composition with alcohol, if As is supposed equivalent to O.

Alcohol. . . $C_4 H_5 O + HO$ or $C_4 H_6 O_2$
Alcarsin. . . $C_4 H_5 As + HO$ or $C_4 H_6 O As$

But as alcarsin is the oxide of a radical cacodyl, $C_4 H_6 As$, pursuing the analogy, alcohol should be the oxide of a corresponding radical $C_4 H_6 O$. Chemists will wait with interest for the investigations of M. Bunsen, illustrative of this point. In the meantime a doubt may be entertained whether the arsenic in alcarsin replaces the oxygen of alcohol, or whether there is any close relation between these two compounds. Their primary binary, or molecular structure is possibly very different. In the ether constituent of alcohol we have probably 4 C zincous or positive, and 5 H + O chlorous. While in cacodyl, we have 4C + As zincous, and 6H chlorous; so that placing the zincous constituent to the left (as usual) and the chlorous to the right, we have the molecular formula for cacodyl as follows:

$$\left.\begin{matrix} C_4 \\ As \end{matrix}\right\} + \left\{\begin{matrix} 3\,H \\ 3\,H \end{matrix}\right.$$

Cacodyl is thus represented as an association of acetyl and arsenietted hydrogen, forming together a compound radical, which is combined in alcarsin, with 1 atom of oxygen and in alcargen with 3 atoms of oxygen.

SECTION VIII.

ON THE RELATION BETWEEN THE ETHYL AND AMMONIUM SERIES.

A remarkable and highly interesting parallelism exists between these two series of compounds, to which the attention of chemists was first directed by Dr. Kane. It will be observed that acetyl has the relation to ethyl, which amidogen has to ammonium, the more compound radical in both cases containing 2 atoms more of hydrogen than the simpler. We may suppose the ethyl compounds to contain acetyl, as the ammonium compounds are supposed, on one view, to contain amidogen; and when thus resolved the analogy of many of the ethyl to ammonium compounds is very striking. The principal difference between the two series depends upon a chemical difference in the characters of their radicals; acetyl being capable of forming acids, while amidogen does not possess that property.

Expressing amidogen NH_2 by Ad, and acetyl $C_4 H_3$ by Ac, the following pairs of compounds from the two series will be found to correspond in composition, differing only in the one containing acetyl while the other contains amidogen. (Liebig's Traité).

TABLE OF CORRESPONDING COMPOUNDS.

COMPOUNDS OF ACETYL.		COMPOUNDS OF AMIDOGEN.	
$Ac = C_4 H_3$	= acetyl	$Ad = N H_2$	= amidogen
$Ac\ H$	= olefiant gas	$Ad\ H$	= ammonia
$Ac\ H_2$	= ethyl	$Ad\ H_2$	= ammonium
$Ac\ H_2\ O$	= ether	$Ad\ H_2\ O$	= oxide of ammonium
$Ac\ H_2\ Cl$	= chloride of ethyl	$Ad\ H_2\ Cl$	= chloride of ammonium
$Ac\ H_2\ Br$	= bromide of ethyl	$Ad\ H_2\ Br$	= bromide of ammonium
$Ac\ H_2\ I$	= iodide of ethyl	$Ad\ H_2\ I$	= iodide of ammonium
$Ac\ H_2\ O + 1$ at. of acid.	= salts of oxide of ethyl	$Ad\ H_2\ O + 1$ at. of acid	= salts of oxide of ammonium
$Ac\ H_2\ O + HO$	= alcohol	$Ad\ H_2\ O + HO$	= compound contained in sulphate of ammonium
$Ac\ H_2\ S + HS$	= sulphydrate of sulphuret of ethyl (mercaptan)	$Ad\ H_2\ S + HS$	= sulphydrate of sulphuret of ammonium
$Ac\ H_2\ O + CS_2$	= xanthic acid	$Ad\ H_2\ S + CS_2$	= sulphocarbonate of ammonium
$Ac\ Pt + Pt\ Cl_2$	= compound of platinum of Zeise (acid)	$Ad\ Hg + Hg\ Cl$	= white precipitate of mercury
$Ac, 2Pt\ Cl + K\ Cl$	= *id.* with chloride of potassium	$Ad, Pt\ Cl + Ad\ H_2\ O$	= base of the platinum salts of Gros
$Ac\ 2Pt\ Cl + Ad\ H_2\ Cl$	= *id.* with sal ammoniac	$Ad, Pt\ Cl + Ad\ H_2\ Cl$	= hydrochlorate of that base
$Ac\ H$	= hydruret of acetyl	$Ad\ H$	= hydruret of amidogen
$Ac\ H + 2SO$	= sulphacetylic acid	$Ad\ H + SO_3$	= anhydrous sulphate of ammonia of Rose

COMPOUNDS OF ACETYL.

$Ac\ O$ = oxide of acetyl
$Ac\ Cl$ = chloride of acetyl
$Ac\ Br$ = bromide of acetyl
$Ac\ O+HO$ = hydrate of the oxide of acetyl (aldehyde)
$Ac\ Cl+H\ Cl$ = chlorhyd. of chlor. of acet. (Dutch liquid)
$Ac\ Br+H\ Br$ = bromhydrate of bromide of acetyl
$Ac\ Cl+Pt\ Cl$ = chloroplatinate of chloride of acetyl (Zeise)
$4Ac+CO$ = ?*
$Ac+Bz$ = oil of cinnamon (Dumas)
$Ac\ Bz+NO_5+HO$ = nitrate of oil of cinnamon
$Ac\ H_2\ O+2C_2\ O_3$ = binoxalate of oxide of ethyl
$Ac\ H_2\ Ad+2C_2\ O_3$ = oxamethane (Dumas)
$Ac\ O+O$ = aldehydic acid
$Ac\ O+O_2 = Ac\ O_3$ = acetic acid

COMPOUNDS OF AMIDOGEN.

$Ad+CO$ = carbamide
$2Ad+2CO$ = urea
$Ad+2CO$ = oxamide
$Ad+Bz$ = benzamide
$Ad\ Bz+C_4\ HO_3+HO$ = hippuric acid

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* $Ac\ CO$ = camphor of the oil of cloves (Dumas) ? santonine (Ettling). $Ac,\ 2CO$ = mannite = $C_8\ H_8\ O+4HO$. Cafein, asparagin, and several other substances also arrange themselves in the series of acetyl.

COMPOUNDS OF ACETYL.

$$\left.\begin{matrix}Ac\,O+\left\{\begin{matrix}Cl\\S\end{matrix}\right.\\ Ac\,O+S_4\end{matrix}\right\}= \text{compounds of Malaguti}$$

$Ac\,Cl+Cl_2=Ac\,Cl_3$ = perchloride of acetyl (Regnault)

Substitutions of the hydrogen of acetyl by chlorine.

$C_4\,H_3\,O+HO$ = aldehyde
$C_4\,Cl_3\,O+HO$ = chloral
$C_4\,H_3\,O_3+HO$ = acetic acid
$C_4\,Cl_3\,O_3+HO$ = chloracetic acid (Dumas)

$C_4\,H_3\,H$ = olefiant gas
$C_4\,Cl_3\,Cl_3$ = deutochloride of carbon
$C_4\,Cl_3\,Cl_3$ = perchloride of carbon corresponding to anhydrous acetic acid
$C_4\,Cl_3+Bz\,Cl$ = chlorocinnose (Dumas.)

COMPOUNDS OF AMIDOGEN.

Substitution of the hydrogen of amidogen.

NH_2 = amidogen
NO_2 = deutoride of nitrogen
NC_2 = cyanogen
$NS_2\,S$ = azoturet of sulphur (Soubeiran), etc.

SECTION IX.

LACTIC AND VISCOUS FERMENTATIONS.

At a temperature between 86 and 104°, the saccharine juices of plants containing albumen or other azotised matter, undergo a species of fermentation, which is different from the vinous, combustible gases being evolved with carbonic acid, and a gummy matter formed, having the composition of gum arabic, which renders the liquid ropy and thick, and hence the application of the name viscous to this fermentation. On examining the liquid after effervescence ceases, it is found to contain no alcohol, but two new substances, in large quantity, namely mannite and lactic acid, which together contain the elements of dried grape sugar, minus 1 atom of oxygen:

$$\begin{array}{ll} \text{Mannite.} \ \ldots\ldots & C_6\,H_7\,O_6 \\ \text{Lactic acid.} \ \ldots & C_6\,H_5\,O_5 \\ \hline & C_{12}H_{12}O_{11} \end{array}$$

MM. Boutron and Fremy have lately observed that the formation of lactic acid precedes that of the other products, and that it may be produced alone, without the evolution of any gas or formation of mannite. Diastase and caseum after they have undergone a modification by a few days' exposure in a humid state, to air, are of all organic matters containing nitrogen the most efficient in determining the lactic fermentation. Air does not interfere by its elements, unless in transforming the animal matter into the lactic ferment. The membranes of the stomach of the dog and calf have no action, when well washed with cold water and fresh, on neutral substances, such as sugar and dextrin, but after being preserved for some time in water, they acquire then the property to transform such matters rapidly into lactic acid. These membranes sometimes produce another acid, differing from the lactic, of which the salt of lime is insoluble in alcohol, while the lactate of lime is readily soluble in that liquid. The substance of bladder after being exposed humid till it begins to decompose, also excites the lactic fermentation.

Diastase after being exposed two or three days to humid air undergoes a modification, and acquire the property of transforming starch into lactic acid, making it pass probably through the intermediate state of dextrin. Hence malt, slightly moistened and exposed to air for two or three days, when afterwards pounded and placed in water kept at a temperature of from 68° to 77°, becomes warm, and after a few days, the liquid is found to contain much lactic acid. This is a pure lactic fermentation, without any production of mannite. But animal matters prepared in a similar manner often modify sugar quite differently, very little lactic acid is formed but considerable quantities of mannite and the viscid matter. Frequently indeed the sugar is wholly changed into alcohol and carbonic acid. The albuminous ferments in different stages of decomposition produce different fermentations. (Annales de Chimie, &c., 3 série, ii, 257.)

LACTIC ACID.

Formula of the acid combined with oxide of zinc: $C_6H_5O_5=\bar{L}$; of the hydrated acid $HO+C_6H_5O_5=HO\bar{L}$,; of the sublimed acid $C_6H_4O_4$.

Other sources of lactic acid, are the whey of milk, in which it is formed while the latter becomes sour, human urine, and probably most other animal fluids, the juice of fermented cabbage or sour-crout, and the fermented extracts of rice and of nux-vomica, the spent ley of tanners, and the sour water of the starch manufacture, from which lactic acid has been prepared for sale.

The process for lactic acid recommended by Boutron and Fremy consists in mixing 8 or 12 pints of milk, with a solution of 8 or 12 ounces of milk sugar in water, and leaving the liquid exposed to air in an open vessel for several days, between 68° and 77°. The liquid being now found very acid, is neutralised with bicarbonate of soda; after twenty four or thirty hours, being again acid, it is saturated, and the saturation repeated till all the milk sugar is converted into lactic acid. When it is supposed that the transformation is complete, the milk is boiled to coagulate the caseum; and the liquid filtered and evaporated to a syrupy consistence, with caution at a moderate temperature. The product of the evaporation is taken up by alcohol at 100°, which dissolves the lactate of soda. Sulphuric acid added in proper quantity to the alcoholic solution, forms sulphate of soda, which precipitates, and the liquid yields by evaporation lactic acid nearly pure. To purify the acid, it may be converted into lactate of lime, which crystallizes immediately in tufts which are perfectly white. From this salt lactic acid may be again separated by means of sulphuric acid. Or, the original lactic acid may be saturated with any other base, and crystallized lactates obtained in a very short time.

Concentrated to a maximum by evaporation, lactic acid is a thick, colourless, uncrystallizable liquid, of density 1.215, without smell, and having a strong sour taste, which is scarcely sensible when the acid is dilute. It is soluble in water and alcohol. Lactic acid dissolves the phosphate of lime, a property which some acids, particularly the acetic, do not possess; it coagulates milk when warmed. When heated to 482° (250° cent.), it undergoes a decomposition, water and several other secondary products appearing, but the principal product being a white crystalline sublimate, of which the composition is $C_6H_4O_4$; that is, anhydrous lactic acid minus 1 atom of water.

This new acid may be purified by dissolving the sublimate in boiling alcohol, from which it precipitates on cooling, in the form of rhomboidal tables, of a brilliant whiteness, which have a weak sour taste, are fusible at 224.6° (107° cent.), and sublime at 482° without alteration. These crystals are very slowly soluble in cold water, but dissolve easily in boiling water; the acid then assumes 2 atoms of water and returns to the condition of hydrated lactic acid.

In the lactates, the single atom of basic water only of the formula is replaced by a metallic oxide; no acid lactates are known, but some basic salts of zinc and the magnesian metals appear to exist, which have not been studied. They are all soluble in water; lactate of zinc is the most sparingly soluble.

Lactates.—No lactate of *oxide of ethyl* has been formed. The lactates of *potash, soda and ammonia* are deliquescent, and do not affect a regular form. The lactate of *barytes* is similar. Lactate of *lime* exists to the extent of 2 or 3 per cent in nux vomica. It crystallizes in colourless needles radiating from a centre, which contain 5 atoms of water of crystallization. Lactate of *zinc* is crystallized by the cooling of a boiling solution, in four-sided prisms, terminated by summits truncated obliquely; they contain 3 atoms of water. Alcohol produces in the aqueous solution a white precipitate of a basic salt, which dissolves in water and crystallizes; it appears to contain 3 atoms of oxide of zinc. Lactate of *magnesia* crystallizes in small plates, containing 3 atoms of water; it dissolves in 30 parts of cold water. The lactates of *alumina, nickel, lead* and *mercury* are very soluble in water, and do not crystallize in a regular form. Lactates of *protoxide of iron*, $FeO,\bar{L}+3HO$, of *oxide of copper*, $CuO,\bar{L}+2HO$, and of *silver* are crystallizable.

Lactate of urea was discovered by MM. Cap and Henry in urine. It may be formed artificially by the double decomposition of lactate of lime and oxalate of urea, the oxalate of lime being separated by a filter, and the liquid evaporated by a gentle heat. The evaporation is terminated in vacuo near concentrated sulphuric acid. Lactate of urea crystallizes in colourless hexagonal needles, of a sharp and cooling taste, which are deliquescent. At a moderate heat it enters into fusion, and sublimes without alteration. Lactate of urea differs from the oxalate and nitrate of urea in not containing 1 atom of water of combination which these possess.

SECTION X.

OIL OF GRAIN-SPIRITS OR FOUSEL OIL, AND BODIES DERIVED FROM IT.

AMYL SERIES OF COMPOUNDS.

Amyl, $C_{10}\,H_{11}=Ayl$; the hypothetical radical of a series of compounds, of which the hydrate of the oxide has long been known as *fousel oil*, or as the *oil of grain-spirits* or *potatoes*, as it is produced in the fermentation of unmalted grain and potatoes, along with alcohol, and distils over with the latter. It has been studied very fully by M. Cahours (An. de Chim. &c. lxx. 81, and lxxv. 193). There is every reason for considering this body as an alcohol, the most striking analogy existing between oil of potatoes and ordinary alcohol. This will be made sufficiently evident by the following table, in which the corresponding compounds of the ethylic and amilic series are compared:

TABLE OF CORRESPONDING COMPOUNDS.

ETHYLIC SERIES.		AMILIC SERIES.	
Alcohol	C_4H_5O,HO	Oil of potatoes	$C_{10}H_{11}O,HO$
Ether	C_4H_5O	Amilic ether	$C_{10}H_{11}O$ (unknown
Chlorhydric ether	C_4H_5Cl	Chloride of amyl	$C_{10}H_{11}Cl$
Bromhydric ether	C_4H_5Br	Bromide	$C_{10}H_{11}Br$
Iodhydric ether	C_4H_5I	Iodide	$C_{10}H_{11}I$
Sulphovinic acid	$HO.C_4H_5O,S_2O_6$	Sulphoamilic acid	$HO.C_{10}H_{11}O,S_2O_6$
Sulphovinate of barytes	$BaO.C_4H_5O,S_2O_6$	Sulphoamilate of barytes	$BaO.C_{10}H_{11}O,S_2O_6$
Acetic ether	$C_4H_5O,C_4H_3O_3$	Acetate of oxide of amyl	$C_{10}H_{11}O,C_4H_3O_3$
Chlorinated acetic ether	$C_4{\genfrac{}{}{0pt}{}{H_3}{Cl_2}}O,C_4H_3O_3$	Chlorinated ditto	$C_{10}{\genfrac{}{}{0pt}{}{H_9}{Cl_2}}O,C_4H_3O$
Olefiant gas (etherene)	C_4H_4	Amilene	$C_{10}H_{10}$
Aldehyde	C_4H_3O,HO	Amilic aldehyde	$C_{10}H_9O,HO$
Acetic acid	$C_4H_3O_3$, HO	Valeric acid	$C_{10}H_9O_3,HO$

HYDRATE OF OXIDE OF AMYL, OIL OF POTATOES, AND OF GRAIN SPIRITS.

Syn. *Fousel oil, amilic alcohol, bihydrate of amylene*; $C_{10}H_{11}O$, HO (Dumas).

In distilling the fermented wash of grain or potato spirits, a milky liquid comes over towards the end of the process, and an oil subsides after a time, which is hydrate of oxide of amyl, mixed with nearly an equal quantity of alcohol and water. To purify the crude product, it is agitated with water several times, left in contact with chloride of calcium for some time, and distilled again. The alcohol and water come off first, and the boiling point of the liquid rises to 269°.6 (132° centig.), when the receiver should be changed, as what then passes over is perfectly pure.

Hydrate of oxide of amyl is a colourless, limpid, oily liquid, of which the odour, at first agreeable, soon becomes rank and nauseous. The inspiration of its vapour occasions spasmodic pains in the chest, with coughing and even vomiting. It burns with a bluish white flame. Its taste is very acrid. It stains paper, but the stain disappears after a time. The density of this liquid is 0.8124 at 59°; its boiling point 269°.6; the density of its vapour 3147, of which the combining measure contains 4 volumes; it freezes at —2 or —4° in crystalline leaflets. Water dissolves a small quantity of it so as to acquire the odour of the oil; it is miscible in all proportions with acetic acid, alcohol, ether, the fat and essential oils. It may be mixed also with solutions of caustic potash and soda; when heated with hydrate of potash, hydrogen gas is given off, and the valerate of potash formed. When distilled with anhydrous phosphoric acid, it yields a liquid hydrocarbon, to which Cahours has given the name of *amilene*.

Hydrate of oxide of amyl unites directly with bichloride of tin, according to Gerhardt, and forms a crystalline compound, which is decomposed by water.

Chloride of amyl, $C_{14}H_{11},Cl = Ayl\ Cl$. This compound is obtained by distilling equal parts of oil of potatoes and perchloride of phosphorus. In a state of purity, it is a colourless liquid, of a pretty agreeable odour, insoluble in water, boiling about 215°.6 (102° centig.), perfectly neutral to test-paper, and having no action upon a solution of nitrate of silver.

Chlorinated chloride of amyl, $C_{10}\genfrac{}{}{0pt}{}{H_3}{Cl_8}Cl$. This substance is the ultimate product of the action of chlorine gas upon the oil in a bottle exposed to the sun, and is formed by the substitution of 8 atoms of chlorine for 8 atoms of hydrogen. It is a colourless liquid, of a strong odour, suggesting that of camphor.

Bromide and *iodide of amyl* were also formed by Cahours. Caustic alkalies dissolved in water attack them with difficulty, but the same bodies dissolved in alcohol decompose these ethers with much facility. The iodide of amyl is produced by distilling at a gentle heat, a mixture of 8 parts of iodine, 15 parts of hydrate of oxide of amyl, and 1 part of phosphorus. The density of its vapour is 6675, and combining measure 4 volumes.

Acid sulphate of oxide of amyl, sulphoamilic acid, is formed when the barytes of the following salt is exactly precipitated by dilute sulphuric acid; it may be evaporated to a syrupy consistence in air or in vacuo, and is sometimes obtained in the form of very fine needles. Its solution is decomposed by heat. When neutralised with bases, it forms a class of salts, the sulphoamilates, which are all soluble in water.

Sulphate of oixde of amyl and barytes, $BaO.\,AylO,\,S_2O_6 + 3\,HO$. This salt is prepared by mixing equal parts of concentrated sulphuric acid and hydrate of oxide of amyl, and neutralising with carbonate of barytes; sulphate of barytes precipitates, while sulphate of barytes and oxide of amyl remains in solution, and may be crystallized by evaporation after being purified by animal charcoal. It forms pearly crystalline leaflets, which are very soluble in water and in alcohol, but scarcely dissolve in ether. The crystals contain 3 atoms of water; when dried at 212° they retain only 2 atoms; the dry salt is decomposed at 392° (200° centig.) Its solution is decomposed by boiling, with escape of hydrate of oxide of amyl.

Sulphate of oxide of amyl and potash forms colourless needles or plates, grouped about a common centre, is very soluble in water and alcohol, and has a very bitter taste.

Sulphate of oxide of amyl and lead crystallizes with 2 atoms of water. Its solution is decomposed by ebullition, like that of the salt of barytes. The salt of *lime* is similar in composition.

Acetate of oxide of amyl, $C_{10}H_{11}O,C_4H_3O_3=AylO,AcO_3$. It is produced by distilling a mixture of 2 parts of acetate of potash, 1 part of hydrate of oxide of amyl, and 1 part of concentrated sulphuric acid. It is a colourless liquid, of an aromatic and ethereal odour, lighter than water, boiling about 257°; insoluble in water, but soluble in alcohol, ether, oil of potatoes, etc. Placed in contact with an aqueous solution of potash, it is altered very slowly; an alcoholic solution of the same base, on the contrary, alters it rapidly, an alkaline acetate is produced, and the oil is regenerated. The density of its vapour is 4475, and combining measure 4 volumes.

Chlorinated acetate of oxide of amyl, $C_{10}\genfrac{}{}{0pt}{}{H_9}{Cl_2}O + C_4H_3O_3$. This compound is formed when the acetate is saturated with chlorine gas at a temperature increasing to 212°. It is a colourless neutral liquid, insoluble in water; and corresponds in composition with the chlorinated acetic ether of Malaguti. It is a liquid body, which becomes yellow, and is altered by a heat above 302°. When exposed again to chlorine gas in sunshine, this liquid absorbs the gas, and a crystalline product is formed containing more chlorine, but which has not been analysed.

Valeric or valerianic acid, $HO,C_{10}H_9O_3$. Oil of potatoes becomes acid when kept in contact with air. M. Cahours has observed, that if platinum black be heated, and the oil be allowed to fall upon it drop by drop in no greater quantity than is imbibed, oxidation occurs, and an acid liquid volatilises, which has all the properties of valerianic acid, the acid obtained by distillation of the root of valerian (*valeriana officinalis*) with water. Two atoms of hydrogen in the oil are replaced by 2 atoms of oxygen. Oil of potatoes corresponds in this respect with alcohol and wood-spirit, which are converted in similar circumstances, by the substitution of 2 atoms of oxygen for 2 atoms of hydrogen, into peculiar acids, the acetic and formic acids. But valerianic acid was first obtained from the oil by MM. Dumas and Stass, by distilling it with hydrate of potash. One part of the oil was covered in a retort by about 10 parts of a mixture of equal parts of hydrate of potash and quicklime; and distilled by a metallic bath at about 392° (200° centig.); hydrogen gas comes over, and valerate of potash is formed. The mass is neutralised by a slight excess of sulphuric acid, and distilled to separate the valeric acid. At the same time, a portion of hydrate of oxide of amyl comes over, accompanied by a liquid having the composition of a *valeric aldehyde.*

Obtained from pure valerate of soda, mixed with a slight excess of phosphoric acid, valeric acid is a colourless oil, lighter than water, and possessed of a persistent and characteristic odour which recals that of the root of valerian, with a sharp and acid taste. The protohydrate produces a white spot on the tongue; its density is 0.937 at 61°.7 (16°.5 centig.); it boils without change at about 347° (175° centig.); it remains liquid at 5°. It inflames easily, and burns with a white and smoky flame. The density of the vapour of this hydrate is 3660 by experiment, 3550 by theory; its combining measure 4 volumes, in which respect it differs from acetic acid. Valeric acid, agrees, however, with that acid in forming a terhydrate, the condition in which valeric acid is always obtained when separated from its salts dissolved in water. Placed in contact with water, valeric acid dissolves a certain quantity of it; the water on its part dissolves the acid considerably.

Valerates.—These salts are in general soluble in water. The valerates of *potash* and *barytes* are not crystallizable. The valerate of *silver* is a heavy crystalline powder, of sparing solubility, which might be confounded, from its appearance, with the fulminate of the same metal.

MM. Dumas and Stass formed two acids by the action of chlorine upon valeric acid, *chlorovalerisic acid,* $C_{10}\begin{matrix}H_6\\Cl_3\end{matrix}O_3+HO$, in which 3 atoms of hydrogen are replaced by 3 atoms of chlorine, and *chlorovalerosic acid,* $C_{10}\begin{matrix}H_5\\Cl_4\end{matrix}O_3+HO$, in which 4 atoms of hydrogen are replaced by 4 atoms of chlorine.—(An. de Chim. lxxiii, 136.)

Amilene, $C_{10}H_{10}$; a liquid hydrocarbon, obtained by distilling hydrate of oxide of amyl repeatedly with anhydrous phosphoric acid. It is colourless, possesses a peculiar aromatic odour, is lighter than water, and contains no oxygen. It boils at 320°; the density of its vapour is 5061 by experiment, and 4902 by calculation, its combining measure 2 volumes.

SECTION XI.

ETHEREAL OIL OF WINES.

The characteristic odour of wine by which it is distinguished from dilute alcohol, is due to a particular substance, possessing the properties of an essential oil. This is common to all wines, and is not to be confounded with the principle which is generally termed the flower, aroma or *bouquet* of individual wines, which is not volatile, and appears to be different in diverse kinds of wine and to be altogether wanting in many kinds.

This oil is less volatile than alcohol, and a small quantity of it is found in the still after the distillation of a large quantity of wine. The same oily liquid is also obtained on distilling the lees of wine, especially what is deposited at the bottom of the tun after the fermentation has begun. It constitutes about $\frac{1}{10000}$ part of wines. This oil belongs to the class of compound ethers, and contains a new acid, which has been named *œnanthic acid*,* in combination with ether; the oil, therefore falls to be named œnanthic ether.

Œnanthic ether, $C_4H_5O,C_{14}H_{13}O_2$. The crude ether contains a variable quantity of free acid in a state of mixture; being more volatile than the acid, the oil may be separated from it by a simple distillation, collecting only the first fourth of the product. To obtain it perfectly pure, it is preferable to agitate the oil frequently with a hot solution of carbonate of soda, which dissolves the free acid without altering the ether. The small quantity of water and alcohol it retains may be withdrawn from it by digestion with chloride of calcium.

The ether purified in this manner, is very fluid, colourless with the odour of wine extremely strong, and almost intoxicating when closely inspired. Its taste is very strong and disagreeable. It dissolves easily in ether and in alcohol, even when the latter is pretty dilute; water does not sensibly dissolve it. Its density is 0.862, its volatility very feeble; it boils between 437 and 446° (225 and 230° centig.); the density of its vapour is by experiment 10508, by calculation 10476.9, its combining measure 2 volumes. Œnanthic ether is instantly decomposed by caustic alkalies, but is not sensibly affected by alkaline carbonates, nor by ammonia. When boiled with caustic potash, it disappears in a few seconds, a considerable quantity of alcohol distils over, and the liquor contains a compound of œnanthic acid and potash, which is very soluble in water.

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* From *οἰνος wine*, and *ανθος flower*.

Œnanthic acid, $HO, C_{14}H_{13}O_2$. When separated from its alkaline combinations, well washed with hot water and dried, this acid, at 55°.7, is of the consistence of butter and perfectly white, but at a higher temperature it melts and forms a colourless oil, without taste or odour, which reddens litmus, dissolves easily in caustic alkalies and in alkaline carbonates. It dissolves easily in alcohol and ether. This acid, like all the fatty acids, forms two series of salts, one acid in composition, without, however, manifesting a sensible acid re-action, the other neutral in composition, which exhibits a well-marked alkaline reaction.

Hydrated œnanthic acid submitted to distillation abandons its water, and becomes anhydrous, $C_{14}H_{13}O_2$, water and a little of the hydrated acid distilling over. The boiling point of the anhydrous acid is more elevated than that of the hydrated acid, as also is the point of fusion of the former; fused anhydrous œnanthic acid becoming solid about 87°.8 (31° centig.)

Œnanthic ether may be reproduced by means of the isolated œnanthic acid. When 5 parts of sulphovinate of potash are heated with 1 part of hydrated œnanthic acid, the mixture fuses; and if it is heated to 302° (150° centig.), an oily liquid is seen to form on its surface, which is a mixture of œnanthic ether and œnanthic acid still free. If this oily layer be separated and heated with a solution of carbonate of soda, the free acid is dissolved and the ether remains in a state of purity.

CHAPTER III.

PRODUCTS OF THE DRY DISTILLATION OF WOOD.

The principal products of the destructive distillation of wood at a red heat, are the charcoal which remains in the retort, gaseous compounds of carbon, a watery fluid containing acetic acid, and a black odorous oily mass, known as tar. The two last products are highly variable mixtures of a great many substances, of which the one that demands our first attention is pyroxylic spirit, or wood spirit.

SECTION I.

METHYL SERIES OF COMPOUNDS.

Formula of methyl, C_2H_3=Me.

A volatile combustible spirit, soluble in water, was first obtained from the dry distillation of wood by Mr. P. Taylor. The composition and chemical nature of this spirit and of the compounds it forms, with their extraordinary parallelism to alcohol and the compounds derived from alcohol, were ascertained by MM. Dumas and Peligot, and published in their important memoir on wood-spirit (An. de Ch. lviii, 5). Wood-spirit is the alcohol of a particular series of compounds, being the hydrated oxide of a new radical methyl, which resembles ethyl perfectly in its functions, but differs in its composition, containing 2 atoms less of carbon and 2 atoms less of hydrogen. The oxide of methyl is a base like the oxide of ethyl or ether, and forms acid and neutral salts like the latter. By the abstraction of 2 atoms of hydrogen from methyl, another radical formyl is produced, as acetyl is derived from ethyl, and having an acid oxide formic acid, corresponding with acetic acid. Methyl has not been isolated.

OXIDE OF METHYL.

Formula C_2H_3O=MeO.

Syn. *Methylic ether.*—This compound is prepared by distilling wood spirit with 4 parts of sulphuric acid, and transmitting the gas which comes over first through a bottle containing milk of lime and afterwards through several bottles filled with pure water. The latter dissolves the oxide of ethyl; the gas is evolved on boiling its solution, and must be collected over mercury. Oxide of methyl is a colourless gas of an agreeable ethereal odour, not liquified by a cold of +3°.2 (—16° cent.), and combustible; water dissolves 37 volumes of this gas, alcohol, hydrate of oxide of methyl and concentrated sulphuric acid much larger proportions. It separates from the latter, on dilution with water; the density of the gas is by experiment 1605, by calculation 1570, and its combining measure 2 volumes.

Oxide of methyl combines directly with the vapour of anhydrous sulphuric acid, in a glass balloon carefully cooled, and forms the neutral sulphate of oxide of methyl (Regnault).

HYDRATE OF OXIDE OF METHYL, OR WOOD SPIRIT.

Formula, $C_2H_3O+HO=MeO+HO$.

Syn. *Pyroxylic spirit.*—In the process of purifying the vinegar from wood, the crude acid is saturated with lime and concentrated by evaporation. The first portion of liquid which distils over contains the wood spirit, which is concentrated by repeated rectification. The wood spirit or pyroxylic spirit of commerce is a heterogeneous mixture, containing besides the hydrate of oxide of methyl which forms the larger part of it, acetone and several other combustible liquids. To purify the wood spirit it is poured over an excess of chloride of calcium in a retort, and distilled by a water-bath heat, which expels acetone and other liquids and leaves the wood spirit united with the chloride of calcium. A measure of water equal to the original volume of the wood spirit is then added to the retort, and the distillation continued; the latter liquid comes over diluted with a small quantity of water, from which it may be separated and obtained anhydrous by another distillation from quicklime.

Wood spirit is a volatile colourless liquid, of an alcoholic but at the same time empyreumatic smell and taste. It is very inflammable and burns with a pale flame like alcohol. It is neutral, mixes when pure with water, without becoming turbid, and is also miscible with alcohol and ether. Its density is 0.798 at 68°; it boils at 140° according to Kane, and at 151°.7 (66°.5 cent.) according to Dumas. The density of its vapour is by experiment 1120, by calculation 1110; its combining measure 4 volumes.

Hydrate of oxide of methyl dissolves, with the aid of heat, small portions of sulphur and phosphorus; it dissolves also many resins, and is used in making spirit varnishes, and mixes with most volatile oils; its solvent power is indeed very similar to that of alcohol. Wood spirit is acted upon by chlorine, peroxide of manganese and sulphuric acid and by other oxidating agents, like alcohol, yielding analogous products. It is also decomposed by potassium, with disengagement of pure hydrogen.

Anhydrous *barytes* is dissolved by pure wood spirit with evolution of much heat, although not dissolved by alcohol, and a compound formed $MeO,HO+BaO$, which crystallizes in needles of a silky lustre. Wood spirit likewise dissolves lime.

Chloride of calcium dissolves in wood spirit and crystallizes from a strong solution in large hexagonal tables, which deliquesce in air; they contain 2 atoms of hydrate of oxide of methyl united with 1 atom of chloride of calcium. Dr. Kane recommends the decomposition of this salt by heat as the best source of pure wood spirit.

Chloride of methyl, $C_2H_3,Cl = MeCl$.—This compound is produced by the reaction of hydrochloric acid and hydrate of oxide of methyl upon each other:

$$MeO+HO \text{ and } ClH=MeCl \text{ and } 2HO.$$

But it is best obtained, as are all the halogen compounds of methyl, by distilling neutral sulphate of oxide of methyl with a metallic salt of the proper salt radical, or better a mixture of sulphuric acid, hydrate of oxide of methyl and the metallic salt. The salt used in the present case is chloride of sodium. Chloride of methyl is a colourless gas of an ethereal odour and sweet taste, of which the density is 1737.8 by experiment, and 1729 by calculation; the combining measure is 4 volumes. Water dissolves 2.8 volumes of this gas at 60°.8 (16° centig.); it is not liquified by a cold of —0.4° (—18° centig.) It will be remarked that the chloride and oxide of methyl are both considerably more volatile than the chloride and oxide of ethyl.

Iodide of methyl, MeI; a colourless liquid, which burns with difficulty, boiling between 104° and 122°; its density is 2.237 at 69.8° (21° centig.)

Fluoride of methyl, MeF; obtained by distilling sulphate of oxide of methyl with fluoride of potassium; a colourless gas, of which the density is 1186; water dissolves 1.5 volumes of it.

Cyanide of methyl, MeCy; an ethereal liquid, insoluble in water.

Sulphuret of methyl, MeS; a very limpid liquid of which the odour is extremely disagreeable. Its density is 0.845 at 69°.8, and its boiling point 105°.8 (41° centig.) The density of its vapour is by experiment 2115, by theory 2158; its combining measure 2 volumes. Sulphuret of methyl is formed, when chloride of methyl is transmitted through an alcoholic solution of protosulphuret of potassium, by double decomposition.

Sulphydrate of sulphuret of methyl or methylic mercaptan is obtained as a colourless liquid, lighter than water, which boils at 69°.8 and acts upon oxides of mercury and lead like sulphhydrate of sulphuret of ethyl (Gregory).

OXYGEN SALTS OF METHYL.

The salts of oxide of methyl correspond so closely with those of ethyl that knowing the history of one class it is easy to predict the properties of the other. Anhydrous metallic oxides do not alter them, while the hydrated alkalies disengage hydrate of oxide of methyl from them with great facility.

Neutral sulphate of oxide of methyl, MeO, SO_3.—This member of the methyl series, which has no analogue in the ethyl series, is formed when oxide of methyl and anhydrous sulphuric acid are brought into contact. It constantly appears also when hydrate of oxide of methyl is distilled with sulphuric acid, and in larger quantity the greater the proportion of sulphuric acid employed. To prepare sulphate of methyl it is convenient to distil 1 part of hydrate of oxide of methyl with 8 or 10 parts of sulphuric acid. When purified by washing with water, and two successive distillations with chloride of calcium and quicklime, sulphate of methyl is a colourless liquid of an alliaceous odour, of density 1.324 at 71°.6 (22° centig.), which boils at 370°.4 (188° centig.), and may be distilled without change. The density of its vapour is 4363.4; it is composed of equal volumes of anhydrous sulphuric acid and oxide of methyl condensed into one volume, so that its combining measure is the same as that of oxide of methyl or 4 volumes. It is decomposed very slowly by cold water, but rapidly by hot water, the acid sulphate of oxide of methyl and water being formed and oxide of methyl liberated. This compound may be employed in preparing all the other compounds of methyl, which are derived from it by double decomposition.

Acid sulphate of oxide of methyl, bisulphate of oxide of methyl, sulphomethylic acid; $HO. MeO + S_2O_6$.—This compound, discovered at the same time by MM. Dumas and Peligot and by Dr. Kane, is formed when concentrated sulphuric acid is mixed with hydrate of oxide of methyl, and also on dissolving the neutral sulphate in boiling water. Obtained by the last method and concentrated by evaporation it is a colourless, syrupy, very acid liquid which in dry air becomes a mass of white crystalline needles. It combines with bases forming double salts, in which the basic water of the acid is replaced by a metallic oxide. All these salts are soluble in water. The double salt of *oxide of ammonium and oxide of ethyl* has not yet been obtained.

Sulphate of oxide of methyl and potash, $MeO.KO,S_2O_6 + HO$ crystallizes in rhomboidal tables, which have the lustre of mother of pearl and deliquesce in damp air. Dr. Gregory has obtained two double salts by dissolving the present salt in a saturated solution of ferrocyanide of potassium, and evaporating; the first which crystallizes yellow and insoluble in alcohol, is a compound of ferrocyanide of potassium and ferrocyanide of methyl; the second a white salt soluble in alcohol is a compound of sulphate of oxide of methyl and potash, bisulphate of potash and cyanide of methyl.

Sulphate of oxide of methyl and barytes, $MeO.KO,S_2O_6 + 2HO$; is prepared by mixing equal parts of concentrated sulphuric acid and hydrate of oxide of methyl, and heating the mixture to its boiling point. After cooling, the liquid is diluted and saturated first with carbonate of barytes and afterwards with hydrate of barytes; the excess of the latter is removed by a stream of carbonic acid gas, and the liquid evaporated to its crystallizing point by a gentle heat. The salt crystallizes in colourless tables of a square base or in thin transparent plates, which effloresce in air and may be made anhydrous in vacuo.

Sulphate of oxide of methyl and lead, $PbO.MeO,S_2O_6 + HO$, is deliquescent. It has likewise been obtained with 2 atoms of water of crystallization and the same form as the preceding salt of barytes (Kane).

Nitrate of oxide of methyl, MeO, NO_5.—The action of nitric acid upon wood spirit is different and much less violent than the action of the same acid upon alcohol. No nitrate of oxide of ethyl is formed, indeed such a compound does not appear to exist, while the nitrate of oxide of methyl is very easily obtained. One part of nitrate of potash and a mixture of 2 parts of concentrated sulphuric acid with 1 part of wood spirit are introduced into a retort; the mass rises greatly in temperature, and the product distils over without the necessity for applying artificial heat; it must be received in a very cold condenser. The heavier of the two liquids found in the receiver is nitrate of oxide of methyl contaminated with a portion of a very volatile compound supposed to be formiate of oxide of methyl, which communicates to the former the odour of hydrocyanic acid. The product is rectified from chloride of calcium and from litharge; the last portions which distil over are perfectly pure. Nitrate of oxide of methyl is a colourless liquid of a weak ethereal odour, which inflames with facility and burns with a yellow flame; its density is 1.822 at 71°.6 (22° centig.), and boiling point 150°.8 (66° centig.) Its vapour heated above 248° is decomposed with a violent detonation, producing carbonic acid, water and deutoxide of nitrogen. This ether is soluble in water, and miscible in all proportions with alcohol, ether and wood spirit.

Neutral carbonate of oxide of methyl is unknown; the *double carbonates* which it forms with alkaline carbonates were prepared in the same manner as the corresponding double salts of ethyl.

Oxalate of oxide of methyl, MeO,C_2O_3, is a white solid transparent and brilliant mass composed of rhomboidal tables; it fuses at 123°.8 (51° centig.), and boils about 321°.8 (161° centig.) It is decomposed by water and resolved into hydrated oxalic acid and wood spirit. *Acid oxalate of oxide of methyl* has not yet been obtained.

Oxalate of oxide of methyl and oxamide or *oxamethylane* is formed when oxalate of oxide of methyl is exposed to dry ammonia.

Sulphocarbonate of oxide of methyl and potash, KO.MeO,C_2S_4.

Bicyanurate of oxide of methyl, $3\,MeO,Cy_6O_6+6HO$, (Richardson).

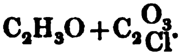
Benzoate of oxide of methyl, $C_2H_3O,C_{14}H_5O_3=MeO,BzO$.

Acetate of oxide of methyl, $C_2H_3O,C_4H_3O_3=MeO,AcO_3$.

Mucate of oxide of methyl, $2C_2H_3O,C_{12}H_{14}O_7=2MeO+\bar{M}u$, (Malaguti).

COMPOUNDS OF OXIDE OF METHYL OF AN UNCERTAIN CONSTITUTION.

Oxichlorocarbonate of oxide of methyl, $C_4H_3ClO_4$; considered by MM. Dumas and Peligot as a compound of oxide of methyl, and a particular acid, and represented by the formula:



$$C_2H_3O+C_2\begin{matrix}O_3\\Cl\end{matrix}.$$

Urethylane, a body corresponding with urethane and formed in similar circumstances.

Sulphate of oxide of methyl and sulphamide, or sulphamethylane, $C_2H_3O,\ SO_3+NH_2,\ SO_2$.

PRODUCTS OF THE DECOMPOSITION OF METHYL AND ITS DERIVATIVES.

A compound belonging to the methyl series was obtained by MM. Dumas and Peligot, which appears to correspond with isethionic acid, by bringing anhydrous sulphuric acid in contact with hydrate of oxide of methyl, observing to keep the mixture cool. Its salt of barytes is crystallizable and has the same composition as sulphate of oxide of methyl and barytes, but does not agree with the latter in its chemical properties, and is evidently a different substance.

Under the influence of air, hydrate of oxide of methyl in contact with platinum black undergoes oxidation, and forms an acid, which is found to be pure formic acid. In this conversion, 2 atoms of hydrogen combine with oxygen and form water, and 2 atoms of oxygen are absorbed at the same time, and combine with the remaining elements of the methyl, exactly as in the conversion of alcohol into acetic acid:

$$C_2H_3O+HO \text{ and } 4O=C_2HO_3+3HO.$$

Formic acid therefore contains a radical, which is named formyl, and to which it has the same relation as acetic acid has to acetyl:

Acetic acid. . . .	$C_4H_3+O_3$.
Formic acid. . .	C_2H+O_3.

Formyl therefore differs from methyl in containing 2 atoms less of hydrogen, and as ethyl may be viewed as a compound of acetyl + 2 atoms of hydrogen, so methyl may be viewed as a compound of formyl + 2 atoms of hydrogen.

SECTION II.

FORMYL SERIES OF COMPOUNDS.

Formyl, $C_2H=Fo$.

The series of formyl is less numerous than that of acetyl. The compounds of the former corresponding to aldehyde and aldehydic acid are deficient, formic acid being the only known oxide of formyl.

The following are the derivatives of formyl:

C_2HO.	Oxide of formyl (unknown).
C_2HO+HO. . .	Substance contained in formomethylal.
C_2HO_3. . . .	Anhydrous formic acid.
C_2HO_3+HO. .	Hydrated formic acid.
C_2HCl_3. . . .	Perchloride of formyl (chloroform).
C_2HBr_3. . . .	Perbromide of formyl.
C_2HI_3.	Periodide of formyl.

COMPOUND OF HYDRATE OF OXIDE OF FORMYL WITH OXIDE OF METHYL, OR METHYLAL.

Syn. *Formomethylal* (Kane) $C_6H_8O_4$ (Malaguti).

By distilling 2 parts of wood spirit with 3 parts of sulphuric acid diluted with 3 parts of water, and 2 parts of peroxide of manganese, Dr. Kane obtained a substance mixed with several other bodies, which he named formomethylal. It was considered a tribasic formiate of oxide of methyl, but was afterwards shown by Malaguti, to be a mixture of formiate of oxide of methyl and a particular substance which he named methylal. To purify the methylal from formiate of oxide of methyl, the latter must be decomposed entirely by hydrate of potash.

Methylal is an ethereal colourless liquid of a very agreeable aromatic odour; it is miscible with 3 parts of water, and may be separated from that liquid by chloride of calcium or hydrate of potash. It is very inflammable, and burns with a white flame. The density of methylal is 0.8551; its boiling point 107.6° (42° centig.); its combining measure contains 4 volumes. Methylal may be represented as a compound of 1 atom of hydrate of oxide of formyl with 2 atoms of oxide of methyl $=C_2HO, HO+2C_2H_3O$. M. Regnault has explained its formation by supposing that 3 atoms of oxide of methyl, formed by the action of sulphuric acid upon hydrate of oxide of methyl, group together so as to form a single molecule$=C_6H_9O_3$; the last exposed to the oxidating action of peroxide of manganese loses 1 atom of hydrogen, which is replaced by 1 atom of oxygen, and consequently the compound $C_6H_8O_4$ is produced. The formation of *acetal* which corresponds with methylal in the acetyl series is explained by Regnault in the same manner.

FORMIC ACID.

Formula $HO+C_2HO_3=HO,FoO_3$.—The relation of this acid to wood spirit has already been explained. It was distinguished as a particular acid by Gehlen, who found it in red ants (*formica rufa*); and was first formed artificially by Dœbereiner, by distilling tartaric acid with sulphuric acid and peroxide of manganese. All other vegetable substance when oxidised in the same manner, or by distillation with nitric acid, hyperiodic, iodic and hypermanganic acids, or with a mixture of chromic and sulphuric acids, yield formic acid, carbonic acid and occasionally some acetic acid.

To obtain the protohydrate in a state of purity, formiate of lead well pulverised contained in a long glass tube is decomposed by a current of dry sulphuretted hydrogen gas; and the disengaged formic acid afterwards distilled over by the application of a gentle heat. This hydrate is a colourless liquid, slightly fuming and possessing a pungent and peculiar odour. It crystallizes below 32° in brilliant plates; it boils at 212°; its density is 1.2353. The vapour of the boiling acid is inflammable and burns with a blue flame; this hydrate combines with a second atom of water forming a definite compound of which the boiling point is 222.8° (106° centig.), which does not freeze at 5°, and of which the density is only 1.1104 at 59°. Both of these hydrates are highly corrosive.

To prepare the dilute acid, a capacious glass retort or copper still is employed, of which the capacity must be at least 10 times greater than the volume of the materials to be employed, namely 1 part of starch, 4 parts of peroxide of manganese, 4 parts of water, and 4 parts of sulphuric acid. The materials without the acid are first introduced into the retort and heated to 104° (40° centig.), and then the sulphuric acid is added by small portions. A violent effervescence with swelling up of the materials occurs, from the disengagement of carbonic acid gas; when this ceases and all the acid is added, the capital is applied to the still, and the distillation continued, for which a heat a few degrees above 212° is sufficient, till 4½ parts of the liquid are found in the receiver. The product is a dilute acid, of which the density is about 1.025; the last portions often contain sulphurous acid, and the product has always an aromatic odour from the presence of a small quantity of a volatile oil formed in the process. The nature of the decomposition which yields formic acid has not been exactly traced. To purify the crude formic acid it is neutralised by milk of lime, which forms an insoluble compound with sulphurous acid; the excess of lime is precipitated by a stream of carbonic acid and the formiate of lime evaporated to dryness. By distilling 10 parts of formiate of lime with 8 parts of oil of vitriol diluted with 4 parts of water, 9 parts of a pure acid are obtained of specific gravity 1.075.

Formic acid is entirely decomposed by an excess of sulphuric acid, without being charred, being resolved into carbonic oxide which comes off with lively effervescence, and water which remains in combination with the sulphuric acid. The acid in question may easily be recognised by that property and also by its action upon the oxides of silver and mercury. When heated upon these oxides formic acid is completely destroyed, producing carbonic acid gas which is disengaged, water and metallic silver or mercury, without leaving the smallest trace of a salt of silver or mercury in the liquor. When the formic acid contains acetic acid, acetate of suboxide of mercury remains in solution. Heated with a solution of corrosive sublimate, formic acid reduces the latter to the condition of calomel, disengaging hydrochloric and carbonic acids; upon the salts of oxides of mercury and silver, formic acid has the same action as upon the oxides themselves. Metallic peroxides are reduced by it with the aid of heat to the state of protoxides, which combine with formic acid, while carbonic acid gas is disengaged.

Formiates.—Formic acid is more powerful than acetic acid; the salts of both acids are all soluble in water. Formiate of soda is not soluble in alcohol like acetate of soda; the formiates comport themselves like the free acid, with sulphuric acid; they also when heated in excess with solutions of salts of silver, mercury, platinum or chloride of gold, precipitate these metals, producing a brisk effervescence. The salts of peroxide of iron are coloured deep orange by a formiate.

Formiate of ammonia, NH_4O, FoO_3, crystallizes in square four-sided prisms; it is very soluble in water. This salt contains the elements of 1 atom of hydrocyanic acid and 4 atoms of water:

$$NH_4O,\ C_2HO_3 = H,\ NC_2 \text{ and } 4HO.$$

It is accordingly converted into these two products when its vapour is carried through a tube at a red heat.

Formiate of oxide of ethyl, formic ether, EO,FoO_3.—This ether is obtained by distilling 7 parts of dry formiate of soda with a mixture of 10 parts of sulphuric acid and 6 parts of alcohol of 90 per cent. It is a limpid liquid of an aromatic penetrating odour and cooling spicy taste. Its density is 0.912; its boiling point 128.12° (53.4° centig.) Formic ether dissolves in 10 parts of water; ammoniacal gas has no action upon it, while solution of ammonia decomposes it like the other alkalies. *Formiate of oxide of methyl* is lighter than water, and boils between 36 and 38° centigrade; its odour suggests that of acetic ether.

Formiate of potash is very soluble and crystallizes with difficulty. *Formiate of soda* crystallizes in prisms of a rhombic base or in tables, containing 2 atoms of water; it is very soluble and deliquescent in damp air. This salt is very suitable for reducing many metallic oxides, when heated with them to redness in the dry way, or when boiled with their solutions. Its solution may be employed to separate the reducible metals from iron, copper, manganese, &c., which are not deoxidised by formic acid.

Formiate of barytes crystallizes in brilliant transparent prisms, which are persistent in air, soluble in 4 parts of water and insoluble in alcohol. Formiate of *strontian* crystallizes in transparent six-sided prisms, containing 4 atoms of water. Formiate of *lime* is soluble in 10 parts of water, and scarcely more soluble with heat than in the cold, so that the best mode of crystallizing it, consists in evaporating its solution by a gentle heat. A concentrated solution of the salt deposits, by evaporation, needles of a brilliant lustre, which effloresce when heated. Formiate of *magnesia* crystallizes in thin brilliant needles, persistent in air, which are soluble in 13 parts of water and insoluble in alcohol. Formiate of *alumina* gives by evaporation a gummy mass which is not crystalline: Its solution with the addition of sulphate of potash, alum, &c., becomes turbid when heated, like acetate of alumina. Formiates of *manganese, protoxide of iron, zinc, cadmium, nickel, cobalt,* and *copper* are very soluble and crystallizable salts.

Formiate of cerium is a white granular and crystalline powder; it is the most insoluble formiate, a property of which advantage is taken in preparing pure oxide of cerium from solutions containing oxide of iron, lime and other oxides. At 392° (200° centig.), this formiate enters into a kind of ebullition and is converted into carbonate of cerium, without charring.

Formiate of lead requires 36 or 40 parts of water for solution, and precipitates when formic acid is added to a saturated solution of acetate of lead, in brilliant needles diverging from a common centre. The solution of formiate of lead has a sweet taste, it is capable of dissolving oxide of lead when boiled upon that oxide and acquires an alkaline reaction. Formiate of lead is insoluble in alcohol.

Formiates of suboxide and oxide of mercury.—Red oxide of mercury well pounded dissolves in formic acid, at the ordinary temperature and forms a solid crystalline mass on evaporating in dry air, which is the formiate of that oxide. On applying the slightest heat to this salt either dry or in solution, effervescence occurs from the escape of carbonic acid, and formiate of suboxide of mercury is produced. The latter salt is deposited from a solution so decomposed, in a crystalline very brilliant micaceous mass, which is composed of small plates of 4 or 6 sides, of a silky or silvery lustre. By a higher temperature formiate of the suboxide is decomposed whether dry or in solution, with a slight explosion, metallic mercury being liberated with formic and carbonic acids. The decomposition of this salt is thus represented by Liebig: 2 atoms of formiate of suboxide of mercury are resolved by heat into:

2 atoms of carbonic acid. . . .	$C_2\ O_4$
1 atom of hydrate of formic acid.	$C_2H_2O_4$
4 atoms of metal.	Hg_4
	$C_4H_2O_8Hg_4$

Formiate of silver is also a salt of sparing solubility. It is obtained by the double decomposition of nitrate of silver with an alkaline formiate, in small leaflets of brilliant whiteness; it is decomposed by heat and resolved into the metal formic and carbonic acids.

Artificial oil of ants, $C_5H_2O_2$ (Stenhouse).—This name was applied by Dœbereiner to the oil which appears in the preparation of formic acid. It was obtained by Dr. Stenhouse in larger quantity than it is produced in the ordinary process, by distilling together equal weights of oatmeal or sawdust and sulphuric acid diluted with its own bulk of water. In the process for formic acid the peroxide of manganese cannot be omitted without greatly reducing the product, but here it is entirely left out. When oil of ants is purified the taste and smell are very pungent and aromatic, resembling oil of Cassia. It catches fire very readily and burns with a strong yellow flame. Its density is 1.1006 at 80.6°, (27° centig.); its boiling point 334.4 (168° centig.) It is pretty soluble in water and more so in alcohol and ether. Potassium decomposes it with effervescence; but neither the aqueous nor the alcoholic solution of potash has any effect upon it.*

COMPOUNDS OF FORMYL WITH CHLORINE, BROMINE AND IODINE.

Protochloride of formyl, $C_2HCl=FoCl$.—One of the substances which Regnault obtained by the action of chlorine upon chloride of acetyl, namely $C_4H_2Cl_2$, is considered by Liebig as protochloride of formyl, its atomic weight being divided by two.

Bichloride of formyl, $C_2HCl_2=FoCl_2$; one of the substances formed by the action of chlorine upon chloride of ethyl, namely $C_4H_2Cl_4$, is so considered by Liebig, its atomic weight being divided by two.

Perchloride of formyl, *chloroform*, $C_2HCl_3=FoCl_3$. This compound is formed in various circumstances. It may be prepared by exposing a mixture of chloride of methyl (C_2H_3Cl) and gaseous chlorine to the direct rays of the sun; by distilling chloral with barytes-water or milk of lime but most conveniently by distilling a dilute solution of chloride of lime with acetone, alcohol or wood spirit. For this purpose 1 part of hydrate of lime is suspended in 24 parts of water, a current of chlorine sent through it till the greater part of the lime is dissolved, and a little milk of lime added to make the liquid alkaline. When the solution of chloride of lime has become clear by repose, $\frac{1}{24}$th of its volume of alcohol is added, and after being left to itself for twenty four hours, the liquid is distilled by a gentle heat in a capacious retort. The product has an ethereal odour, and contains perchloride of formyl mixed with alcohol, on shaking it with water the perchloride separates as a dense liquid, and may be obtained perfectly pure by digesting it upon chloride of calcium, and distilling it again with concentrated sulphuric acid. (Liebig's Traité).

Perchloride of formyl is a colourless oily liquid, of an agreeable ethereal odour and sweetish taste; its density is 1.480 at 64.4° (18° centig.); its boiling point 141.44° (60.8° cent.) It is inflamed with great difficulty but burns in the flame of a candle colouring it green. The alcoholic solution of potash destroys it, converting it into formiate of potash (Dumas), a property which the name chloroform refers to:

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* Dr. Stenhouse, Phil. Mag., 3rd Series, vol. 18, p. 122.

$$FoCl_3 \text{ and } 4KO = KO, FoO_3 \text{ and } 3KCl.$$

The density of its vapour is by experiment 4200, by calculation 4116: its combining measure 4 volumes. Chloroform may be distilled from sulphuric acid, potassium or potash without being sensibly altered. Exposed with chlorine to the direct rays of the sun it is decomposed and converted into hydrochloric acid and a particular *chloride of carbon* C_2Cl_4, which boils at 172.4° (78° centig.), and of which the density of the vapour is 5300, and combining measure 4 volumes (Regnault). This chloride of carbon has been looked upon as a formic acid in which both the hydrogen and oxygen are replaced by chlorine:

$$C_2Cl + Cl_3;$$

while the well known sesquichloride of carbon is related in the same way to acetic acid:

$$C_4Cl_3 + Cl_3.$$

When the former chloride of carbon is made to pass in vapour through a porcelain tube at a dull red heat, it is divided into two new chlorides of carbon, of which the composition is expressed according to M. Regnault, by CCl and CCl_3.

Chlorhydrate of chloride of formyl, $2C_2HCl, HCl$; one of the products of the action of chlorine upon the chlorhydrate of the chloride of acetyl.

Perbromide of formyl, bromoform, $C_2HBr_3 = FoBr_3$; prepared like the perchloride, and very analagous to it in properties; its density is 2.10. It is less volatile than the perchloride, and more easily decomposed by alkalies.

Periodide of formyl, iodoform, $C_2HI_3 = FoI_3$.—This is a yellow volatile substance discovered by Serullas, which is often described as an iodide of carbon. It is obtained on adding an alcoholic solution of potash to a solution of iodine in alcohol, till the last is discoloured, carefully avoiding any excess of alkali. The alcohol is then expelled by gentle evaporation, and the iodide of formyl is deposited in crystals, which are purified from iodide of potassium by washing with pure water. This compound is formed in consequence of the decomposition of 1 atom of alcohol and 6 atoms of potash, by 8 atoms of iodine, by which 1 atom of periodide of formyl, 1 atom of formiate of potash, 5 atoms of iodide of potassium and 4 atoms of water are produced (Liebig).

$$\begin{array}{llllll}
\text{1 atom of alcohol.} \;.\;.\;.\; & C_4\left\{\begin{matrix} H\;O \\ H_5O \end{matrix}\right\} & & & & \\
\text{8 atoms of iodine.} \;.\;.\;. & & & I_8 & \\
\text{6 atoms of potash.} \;.\;. & & O_6 & & K_6 \\
\hline
 & C_4 & H_6O_8 & I_8H_6 & \\
\end{array}$$

Equivalent to:

$$\begin{array}{ll}
\text{1 atom of periodide of formyl.} \;.\;.\;. & C_2H \quad\; I_3 \\
\text{1 atom of formiate of potash.} \;.\;.\;. & C_2H\;O_4\;\;K \\
\text{5 atoms of iodide of potassium.} \;.\;. & \qquad\; I_5K_5 \\
\text{4 atoms of water.} \;.\;.\;.\;.\;.\;.\;. & \quad H_4O_4 \\
\hline
 & C_4H_6O_8I_8K_6 \\
\end{array}$$

Iodoform crystallizes in brilliant yellow plates, and has a characteristic odour suggesting that of saffron. It is insoluble in water, but very soluble in alcohol, ether and wood spirit. It sublimes at 212°; at 248° it undergoes decomposition and is resolved into carbon, iodine and hydriodic acid. It gives a peculiar liquid of a deep red colour and density 1.96, when distilled with chloride of phosphorus or with corrosive sublimate; this liquid contains chlorine, iodine and formyl.

Sulphuret of formyl, FoS_3? (Bouchardat). A liquid obtained by distilling 1 part of iodide of formyl with 3 parts of sulphuret of mercury; hydrate of potash converts it into sulphuret of potassium and formiate of potash.

Action of chlorine upon oxide of methyl.—Chlorine gas decomposes the oxide of methyl gas, forming hydrochloric acid and the following products, as observed by M. Regnault:

		Density.	Boiling point.	Density of vapour.
Oxide of methyl.	C_2H_3O			1570=2 v.
Monochlorinated oxide of methyl.	$C_2\genfrac{}{}{0pt}{}{H_2}{Cl}O$	1.315	105° cent.	4047=2 v.
Bichlorinated oxide of methyl. . .	$C_2\genfrac{}{}{0pt}{}{H}{Cl_2}O$	1.606	130° „	6367=2 v.
Perchlorinated oxide of methyl. .	C_2Cl_3O	1.594	212° „	4670=4 v.

The combining measure of perchlorinated oxide of methyl differs, it will be observed, from the other members of the series. (Annales de Chimie, etc. lxxi. 353).

Chlorine is absorbed with great avidity by hydrate of oxide of methyl and a heavy oil formed, which has not yet been fully examined.

Action of chlorine upon chloride of methyl.—This also gives rise to a series of compounds, in which the proportion of chlorine increases as the action is prolonged. (Regnault).

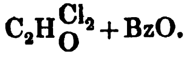
		Density.	Boiling point.	Density of vapour.
Chloride of methyl.	C_2H_3Cl			1738=4 v.
Monochlorinated ditto. . . .	$C_2H_2Cl_2$	1.344	30.5° cent.	3012=4 v.
Bichlorinated do. (chloroform).	$C_2H\,Cl_3$	1.491	60.8° „	4230=4 v.
Perchlorinated ditto.	C_2ClCl_3	1.599	78° „	5245=4 v.

The monochlorinated chloride of methyl has an odour which is very sharp and is similar to that of Dutch liquid; treated with an alcoholic solution of potash, the former liquid gives only a very trifling precipitate of chloride of potassium, and distils over almost entirely without change.

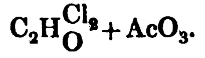
The perchloride of carbon, C_2Cl_4, which is named above perchlorinated chloride of methyl, is not altered by a solution of hydrosulphuret of the sulphuret of potassium. It is decomposed by heat and gives different chlorides of carbon according to the temperature.

At a dull red heat, this chloride C_2Cl_4 appears to be converted into another chloride of carbon C_2Cl_3, supposing the combining measure of the latter to be 4 volumes, its density being 4082. This new chloride of carbon will therefore be isomeric with Faraday's sesquichloride C_4Cl_6, but of only half the density. When decomposed at a higher temperature it gives small silky crystals of the chloride of carbon of Julin CCl. Lastly at a bright red heat the liquid chloride of carbon C_4Cl_4 is the principal product.

Chlorine acts readily upon the sulphuret of methyl and upon the compounds of oxide of methyl with acids or the compound methylic ethers. A benzoate and acetate of an oxichloride of formyl have been produced, having the following formulæ, (Malaguti):



$$C_2H\overset{Cl_2}{\underset{O}{}}+BzO.$$



$$C_2H\overset{Cl_2}{\underset{O}{}}+AcO_3.$$

A mixture of iodine, nitric acid and wood spirit left to itself for a long time, deposits yellow crystals. Bromine in the same circumstances gives a heavy oily liquid (Aimé).

SECTION III.

PRODUCTS OF THE DISTILLATION OF WOOD HAVING SOME RELATION TO OXIDE OF METHYL.

Xylite, lignone (Gmelin), a liquid which exists in commercial pyroxylic spirit, and is separated from the hydrate of oxide of methyl by distillation from chloride of calcium at 212°. MM. Weidmann and Schweizer, in their last memoir on these products, assign to xylite the formula $C_6H_6O_{2\frac{1}{2}}$. The density of its vapour was by experiment 2177, by theory 2159; its boiling point 142.7° (61.5° centig.); density 0.816. Pure xylite has an agreeable, sharp odour, and empyreumatic taste. It is miscible with water, dissolves but little chloride of calcium, and burns with a white flame.

Mesiten, $C_6H_6O_3$ (Weidmann and Schweizer), a liquid obtained by distilling equal parts of sulphuric acid and xylite, in which chloride of calcium is wholly insoluble. Its density is 0.808; boiling point 145.4° (63° centig.)

Xylitic acid, $C_4H_3O_{1\frac{1}{2}}$ (W. and S.), obtained by treating anhydrous xylite with hydrate of potash. The salt thus formed is supposed to be a compound of xylitate of potash with xylite, $3\,(KO,\,C_4H_3O_{1\frac{1}{2}})+C_6H_6O_{2\frac{1}{2}}$. It is readily soluble in wood-spirit, but is insoluble in anhydrous xylite. Xylite oil and xylite resin are two other substances contained in an oil, formed, among other products, by the action of an excess of hydrate of potash upon xylite.

Mesite, $C_6H_6O_2$ (W. and S.). This liquid which, in its physical properties, very much resembles mesiten, exists in crude proxylic spirit, and comes over late in its rectification. Mesite may, therefore, be separated, by distillation with water, from xylite, as the latter passes over early. Mesite is also formed by the action of potash and potassium upon xylite. It is colourless, volatile, and of an ethereal odour, boils somewhat above 158°, and is soluble in water.

Xylite naphtha, $C_6H_6O_{1\frac{1}{2}}$.—By the action of hydrate of potash upon mesite, acetic acid is formed and xylite naphtha. When pure, this liquid is colourless and very fluid, having an odour resembling oil of peppermint, but slightly soluble in water, soluble easily in alcohol, wood-spirit, xylite and ether. It boils at 230°, and burns with a white and smoky flame.

The principal products of the treatment of xylite-naphtha by an excess of hydrate of potash or potassium are xylite-oil and xylite-resin.

Xylite-resin, $C_{24}H_{18}O_3$; when pure, is a reddish, brown, brittle mass, fusible under 212°, but decomposed by a higher temperature. It is insoluble in water, or in solution of potash, and gives no precipitate with an alcoholic solution of acetate of lead. It is readily dissolved by alcohol, wood-spirit, xylite and ether.

Xylite-oil, $C_{12}H_9O_1$. To obtain this oil pure, it is necessary to act upon xylite with a great excess of hydrate of potash. It is colourless, but usually yellow, lighter than water and nearly insoluble in it, readily dissolved by alcohol, etc. It has a bitter, burning taste, a peculiar odour, boils considerably above 392° (200° centig.), and may be distilled without decomposition. It burns with a white, very smoky flame. When decomposed by hydrate of potash, xylite-oil gives acetic acid and a peculiar *resin*, $C_{48}H_{36}O_3$; not so fusible as xylite-resin.

When 1 part of anhydrous acetone is gradually mixed with 2 parts of hydrate of potash, well pulverised, the vessel being kept cool, and the mass mixed after six or eight days with water, a brown oily liquid separates; this may be washed with water to free it from undecomposed acetone, and distilled with water to separate it from a resinous body. This oil has the same boiling point and composition as xylite-oil, and appears to be identical with it. The resin has also the same composition as xylite-resin.*

Methol, $C_{12}H_9$; a liquid produced by the distillation of xylite with sulphuric acid; pure wood-spirit does not yield it, although it was first obtained by the treatment of the crude spirit; it is a hydrocarbon, and contains no oxygen. It does not mix with sulphuric acid, but by long digestion and agitation, it disappears entirely, and is partly converted into a black *resin*, $C_{24}H_{16}O$, which is insoluble in alcohol and wood-spirit, but soluble in ether and xylite. Methol is not converted into this resin by the action of air. The acid solution neutralised with carbonate of lime gives a white crystalline salt, containing *methol-sulphuric acid*, of which the formula when free is $HO,SO_3 + C_{12}H_9, SO_3$, or perhaps rather $HO, C_{12}H_8S_2O_5 + HO$.*

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* Lœwig and Weidmann; Poggendorff's Annalen, l, 299.

Mr. Scanlan has shown that crude wood-spirit contains free *aldehyde*, which he has extracted from it in a state of purity by submitting the crude spirit to successive distillations. L. Gmelin obtained *acetone* from the wood-spirit of the French manufactories; it distilled over first when the crude spirit was rectified from chloride of calcium.

Pyroxanthin, eblanin,† $C_{21}H_9O_4$ (Gregory and Apjohn); a crystalline substance of an orange colour, obtained by Mr. Scanlan on distilling crude pyroxylic spirit from slaked lime. It remains with the lime, and after neutralising the latter with acetic acid, may be taken up by alcohol, from which it is deposited in long needles or prisms having the colour of carbazotate of potash. It is insoluble in water and in alkalies, but soluble in alcohol, ether and concentrated acetic acid. It sublimes at 273°, but does not melt till it is raised to the temperature of 291°. Concentrated sulphuric acid dissolves it and assumes a red blue colour.‡

SECTION IV.

OTHER PRODUCTS OF THE DISTILLATION OF WOOD, CONTAINED IN TAR.

Paraffin is a particular hydrocarbon, produced in the distillation of wood, and in many other circumstances, which has the same composition per cent as olefiant gas, or CH. It is a crystalline substance, transparent and colourless, soft and not unlike stearic acid, inodorous and tasteless, fusible at 110.6° (43.75° centig.), and capable of being distilled at a higher temperature without alteration. A cotton-wick which has imbibed melted paraffin, burns without smoke or odour, like a wax taper. Its density is 0.870.

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* F. Weidmann and E. Schweizer; Poggendorff's Annalen, xliii, 593; xlix, 135 and 293; l, 265.

† From Eblana, Dublin.

‡ Liebig's Annalen for 1837; or Dr. Thomson's Organic Chemistry, Vegetables, p. 750.

In a chemical point of view, paraffin is distinguished for a remarkable indifference to other bodies; hence the name paraffin *(parum affinis)* assigned to it by M. Reichenbach, its discoverer. It is not decomposed by chlorine, by alkalies or acids. Paraffin is very soluble in ether and oil of turpentine; boiling alcohol dissolves only 3.45 per cent of its weight. This and the other principles existing in tar are obtained by long and intricate processes, which cannot be shortly described.*

Eupion, C_5H_6, is best obtained from animal tar. It is a colourless, very limpid liquid (whence its name), without odour or taste, of density 0.655, not frozen by —4°, boiling at 336.2° (169° centig.), and distilling over without change. It burns easily by means of a wick, with a bright flame and no smoke. Eupion is insoluble in water, but soluble in alcohol. It is not altered by potassium, by chlorine or iodine, which it dissolves, nor by acids or alkalies.—(Reichenbach, Ann. de Chim. l, 69.)

Creosote, $C_7H_{4\frac{1}{2}}\dot{O}$ (Ettling), is present in wood-smoke, in tar, and generally in wood-vinegar (pyroligneous acid), to which it communicates its odour, taste and antiseptic properties. It is an oily colourless liquid, of high refracting power, of which the odour is penetrating and disagreeable, analogous to that of smoked meat, and the taste burning and very caustic. Its density is 1.037 at 68°; it boils at 397.4° (203° centig.), and is not frozen by a cold of —16.6° (—27° centig.). It burns with a very smoky flame.

Creosote forms two different compounds with water at the ordinary temperature; one is a solution of 1.25 parts of creosote in 100 parts of water; the other, on the contrary, a solution 10 parts of water in 100 of creosote. Acetic acid appears to be a special solvent of creosote; these two liquids mix in all proportions. Potassium is decomposed in it with effervescence and formation of potash. Creosote forms in the cold two com-

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[*] Reichenbach; Ann. de Chimie, etc. t. 30, p. 69. Also Dr. Thomson's Organic Chemistry, Vegetables, p. 723; or Traité de Chimie, par M. Dumas, t. v. p. 652.

pounds with potash; one is anhydrous, liquid, of an oily consistence, the other hydrated and crystallized in white pearly plates; they are both decomposed by all acids, even carbonic acid. It mixes in all proportions with alcohol, ether, sulphuret of carbon, oil of petroleum and acetic ether. Creosote is remarkable for dissolving a large number of organic colouring matters, including cochineal, dragon's blood, litmus, madder, saffron, and even indigo, when heated. It coagulates albumen, a property upon which its corrosive action upon animal tissues may depend. Butcher-meat or fish dipt in it, and then exposed to air, does not putrify,* but acquires the agreeable flavour of the same kind of food when well smoked.

Picamar (*in pice amarum*) is a transparent and nearly colourless liquid, of the consistence of an oil somewhat thickened; its odour is weak and peculiar, its taste insupportably bitter and burning, then cooling, like that of peppermint. Its density is 1.10 at 68°; its boiling point 518°. It is the bitter principle, according to M. Reichenbach, of all empyreumatic products. It forms crystalline compounds with the alkalies and alkaline earths, in which the latter are not neutralised. It is insoluble in water, but soluble in alcohol and ether.

Pittacal, a beautiful colouring matter, discovered by Reichenbach in the oil of tar; the latter substance, when free from acid, assuming a beautiful blue on the addition of barytes-water to it. This substance when precipitated or obtained by evaporation forms a deep blue mass, solid and friable, like indigo. It assumes also a coppery lustre, like indigo, when rubbed. It is inodorous, insipid and not volatile. Pittacal is insoluble in water, but is suspended in that liquid in a state of such minute division as to pass through a paper filter, and colour the liquid blue. Its solution in acetic acid is of a rose red colour, and recovers a very fine blue colour on the addition of an excess of alkali. M. Reichenbach recommends it as a re-agent even more sensible than litmus to the action of acids and alkalies. It is not soluble in alcohol, ether or eupion. It is not altered by air and light.

Pittacal gives precipitates of a fine violet blue colour, with acetate of lead, chloride of tin, ammoniacal sulphate of copper and acetate of alumina. This substance may be available ultimately, in the opinion of M. Reichenbach, as a colouring matter in dyeing.

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* Hence the name creosote, from κρεας flesh, and σοζω I save.

Besides the bodies described, other substances have been found among the products of the distillation of wood, to which the names *cedriret*, *chrysene*, *pyrene* and *capnomor* have been given.

PRODUCTS OF THE DISTILLATION OF COAL.

The general products of the distillation of coal, which appear in gas-making, are: 1, the residuary carbon or coke; 2, gaseous compounds of carbon and hydrogen, including olefiant gas (page 422); 3, a watery liquid, containing salts of ammonia; and, 4, tar.

When the tar is distilled with water, an oily liquid comes over, and there remains behind a black resinous substance, or pitch, of the nature of which little is known. The oil is a mixture of several bodies, some of which are capable of combining with bases, and some with acids. Particular substances have been isolated, to which the names, *leucol*, *pyrrol*, *cyanol*, *carbolic acid*, *rosolic* and *brunolic acids* are applied, but the most remarkable product in coal-tar is *naphtaline*, which is sometimes found sublimed pure, in white crystalline plates, in the gas apparatus.

NAPHTALINE.

Formula: $C_{20}H_8$. M. Laurent has observed that this substance is best obtained from tar which is somewhat old. The tar is boiled in air till it is deprived of water, and then distilled in a retort with a copper adopter or connecting tube, and glass receiver. The first portion of oil distilled is of a yellowish colour, which becomes dark coloured in air, and allows much naphtaline to fall when cooled to 14° or 10° Fahr. If re-distilled, and the last portions received apart, they yield naphtaline in large quantity when cooled. To purify naphtaline, it is crystallized twice from alcohol, taking care to press the crystals each time in folds of cotton cloth. If the oil is submitted for some time to a current of chlorine, it yields afterwards an increased product of naphtaline.

Naphtaline is in transparent and colourless plates, has a strong peculiar and not unpleasant odour, a burning aromatic taste, is denser than water, insoluble in it, melts at 176°, boils at 422.6° (217° centig.), and condenses in shining leaflets. The density of its vapour is 4528 by experiment, and 4488 by calculation; its combining measure is 4 volumes. Naphtaline burns, when heated, with a white smoky flame. It is very soluble in alcohol and ether, and crystallizes from these solutions on dilution with water. Naphtaline is peculiarly the product of a high temperature, and is furnished by alcohol and organic matters in general when heated to redness.

Naphtaline dissolves in concentrated sulphuric acid, upon the application of heat; with anhydrous sulphuric acid it combines when heated, and forms a fine purple red liquid. The compound contains three peculiar acids, which on diluting the mass with water and neutralising it with carbonate of barytes, are obtained in three different barytes salts, which may be separated and distinguished from each other by their unequal solubility and different crystallization. They are:

Naphtalin-hyposulphuric acid or *sulphonaphtalic acid*, $HO + C_{20}H_8S_2O_5$. It is soluble in water and crystallizes, is sour and bitter, with a metallic after-taste. The hyposulphuric acid it contains is not neutralised by the naphtaline, and combines with the usual proportion of base to form a neutral salt. *Sulphonaphtalate of barytes* $BaO + C_{20}H_8,S_2O_5$, crystallizes in brilliant light spangles, burns in the flame of a candle, is insoluble in alcohol. It parts with an atom of water when heated; its formula may then be $BaO + C_{20}H_7,S_2O_4$.

Naphtin-hyposulphuric acid or *sulphonaphtic acid*, $HO + C_{11}H_{4\frac{1}{2}}O,S_2O_5$, is not crystallisable, and very soluble in water.

Glutinhyposulphuric acid is separated from its salts by hydrochloric acid as a milky substance, which falls and collects together in transparent, clammy drops; its salts do not crystallize.

When naphtaline is dissolved in excess by sulphuric acid, and water added, the excess is precipitated, but in an altered state, for when the precipitated naphtaline is distilled with water, it leaves behind a fatty matter, from which alcohol separates two new compounds, *sulphonaphtaline*, $C_{20}H_8$, SO_2 and *sulphonaphtalide*, $C_{24}H_{10}$, SO_2. Both are inodorous and insoluble in water.

By the action of chlorine upon naphtaline, two compounds of that substance with chlorine in different proportions are formed; and by the abstraction of hydrochloric acid from these, or continued action of chlorine, several other compounds are produced:

1. $C_{20}H_8Cl_2=C_{20}H_7Cl + H\,Cl$
2. $C_{20}H_8Cl_4=C_{20}H_6Cl_2+H_2Cl_2$
3. $C_{20}H_6Cl_2=C_{20}H_6Cl_2$
4. $C_{20}H_6Cl_6=C_{20}H_4Cl_4+H_2Cl_2$
5. $C_{20}H_5Cl_3=C_{20}H_5Cl_3$

The first of these compounds *chlorhydrate of chloro-naphtalase* of Laurent is formed when naphtaline absorbs chlorine gas at the usual temperature; it is a yellow oil, denser than water and insoluble in it. When treated with potash it loses HCl, and gives the *chloronaphtalase* of Laurent, $C_{20}H_7Cl$.

The second, *chlorhydrate of chloronaphtalese* of Laurent, when naphtaline is saturated with chlorine gas at 140°. It crystallizes from ether in transparent rhomboidal tables, requires a temperature of 320° to fuse it, and forms a crystalline mass on cooling.

The third, *chloronaphtalese* of Laurent, is produced by the distillation of the second, or by treating it with an alcoholic solution of potash, with the separation of 2 atoms of hydrochloric acid. It crystallizes from alcohol in rhombic prisms, is tasteless and inodorous, and fuses at 111.2° (44° centig.). Two other isomeric compounds of the same formula exist, one an oil, the other obtained by potash.

The fourth compound, *chlorhydrate of chloronaphtalose* of Laurent, is produced by the action of chlorine gas upon the third, at the usual temperature. It much resembles the body from which it is derived, fuses at 105.8° (41° centig.), and may be sublimed without change.

The fifth compound, *chloronaphtalise* of Laurent, is the product of the action of chlorine on the first or fluid chloride of naphthaline in sunshine, or with heat and subsequent distillation of the oil formed. It crystallizes from ether in large striated prisms, which are colourless, inodorous, soft like bees'-wax, fusible at 163°.4 (73° centig.). This compound is a naphtaline in which 3 atoms of hydrogen are replaced by 3 atoms of chlorine. (Laurent, Ann. de Chim. &c. lxvi, 196).

M. Laurent has obtained two neutral substances and two acids, from the action of nitric acid upon the naphtalic chlorides (Ann. de Chim. lxxiv, 26):

Oxichloronaphtalose .	$C_{20}H_4Cl_2O_2+HO$
Chloronaphtalosic acid .	$C_{20}H_4Cl\ O_3+O_2$
Naphtalosic acid	$\frac{1}{2}(C_{16}H_4O_4\ \ +O_2)$
Oxichlorophtalenose . .	$C_{18}H_4Cl_3O$

Nitronaphtalide (*nitronaphtalase*), $C_{20}H_7+NO_4$, is produced on heating naphtaline with nitric acid, by the separation of HO. It crystallizes from alcohol in four-sided prisms, of a sulphur-yellow colour, fuses at 109°.4 (43° centig.), and may be sublimed when cautiously heated; when suddenly heated it burns.

Nitronaphdehyde (*nitronaphtalese*), $C_{20}H_6+2NO_4$, is formed by boiling the former compound, or naphtaline and nitric acid till no oily body floats on the surface of the liquid. It falls upon the cooling of the liquid as a yellow crystalline powder, fusible at 365°, which may be sublimed without change, and is insoluble in water and alcohol. (Laurent).

The action of nitric acid on naphtaline being continued for a longer time and at a high temperature, after the expulsion of the nitric acid in nitrous fumes and the sublimation of the naphtalese, a feeble explosion takes place, and a coaly mass remains in the retort. By repeating the treatment of this mass with nitric acid, M. C. de Marignac obtained the three following new products: 1, *Nitronaphtalise*, $C_{20}H_{10}N_3O_{12}$ or $C_{20}H_{10}+3NO_4$; a yellow, glutinous, resinous substance, insoluble in water, dissolved out of the mass by ether. This substance is named by Marignac according to the plan followed by Laurent of distinguishing compounds obtained successively from the same root by the vowels, *a*, *e*, *i*, *o*, etc.; the two preceding compounds being nitronaphtalase and nitronaphtalese, this falls to be named nitronaphtalise. Alkalies decompose this substance, and convert it into—2, a *brown matter*, $C_{12}H_3NO_5$, carbonic acid and ammonia; 3, *nitronaphtalic acid*, $2HO+C_{16}H_5NO_{12}$; a bibasic acid, soluble in water, forming crystallizable salts. The salt of *ammonia* is white, with the lustre of mother of pearl, and resembles the crystalline plates of naphtaline; it is readily dissolved by water, and pretty soluble in alcohol. The salts of *silver* and *barytes* contain two atoms of metallic oxide, the salt of *lead* four atoms.

M. de Marignac also obtained a *volatile liquid*, which distilled over with the excess of nitric acid, in treating the hydrochlorate of chloronaphtalese ($C_{20}H_8Cl_4$) with that acid, of which the constitution is remarkably simple, $C\ Cl\ NO_4$, or $C\ Cl+NO_4$. This liquid, which is not named, is perfectly colourless, transparent, of density 1.685 at 59°, of an odour excessively irritating, like that of chloride of cyanogen, and affecting the eyes, neutral to test-paper. Water dissolves a mere trace of it, but acquires thereby its smell and taste. It dissolves easily in alcohol and ether; nitric and hydrochloric acids dissolve only a very little of it. Its boiling point appears to be not greatly above 212°. The aqueous solution of potash has no action upon it, the alcoholic solution dissolves it easily, and after a time, a crystalline potash-salt falls, which is decomposed when heated, with explosion. The density of its vapour was not ascertained.

The *naphtalic acid*, which is formed and remains in the retort in the preceding process, did not possess the properties or composition of the acid which M. Laurent obtained by a similar process. Marignac's naphtalic acid contains nitrogen, with carbon and hydrogen in the proportion of C_8H_5, which is inconsistent with the formula of the following acid.*

Naphtalic acid, $HO+C_8H_2O_3$, is formed on heating with nitric acid the second compound or solid chloride of naphtaline in the foregoing list (the chlorhydrate of chloronaphtalese); ruddy fumes are given off, and the acid solution gives on concentration a white crystalline crust, which is naphtalic acid. One equivalent of chlorhydrate of chloronaphtalese and 10 equivalents of oxygen give 2 equivalents of naphtalic acid, 2 equivalents of oxalic acid, and 4 of hydrochloric acid:

$$C_{20}H_8Cl_4 \text{ and } 10O = 2C_8H_2O_3 \text{ and } 2C_2O_3 \text{ and } 4HCl.$$

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* C. de Marignac, in Liebig's Annalen, vol. 38, pp. 1 & 13.

It crystallizes by sublimation in long thin prisms, resembling benzoic acid, which are inodorous, have a weak taste, fuse at 221°, are soluble with difficulty in water, have an acid re-action and form salts with bases. (Laurent.)

Paranaphtaline, $C_{30}H_{12}$; accompanies naphtaline in tar, and is deposited by the distilled oil when greatly cooled in crystalline grains. It is distinguished from naphtaline by its sparing solubility in boiling alcohol. It is also less fusible and less volatile, fusing at 356° and boiling above 572° (300° centig.). Its best solvent is oil of turpentine. It contains carbon and hydrogen in the same proportion as naphtaline, but on taking the density of its vapour, it is found that 3 volumes of naphtaline represent only 2 of paranaphtaline; the density of the latter is 6732. (Dumas and Laurent, Ann. de Chim. l, 187).

SECTION V.

BITUMEN.

A tarry matter, known as bitumen, is found native in various parts of the world, sometimes so consistent as to be termed pitch or asphalt, and often liquid and thin, as the native petroleum or naphtha of Persia and Rangoon. The latter, however, always holds much fixed matter in solution.

According to the recent observations of MM. Pelletier and Walter, natural naphtha consists of several liquid and one solid compound, paraffin namely, which it contains ready formed. The liquid compounds are hydrocarbons, which these chemists name naphtha, naphtene and naphtol. They are separated from each other by distillation, as they have different boiling points.

Naphtha, $C_{14}H_{13}$; boils between 185° and 194°, is decomposed by sulphuric and nitric acid, particularly with the aid of heat, less affected by chlorine; iodine dissolves in it. The density of its vapour is by observation 3400, by calculation 3390.

Naphthene, $C_{16}H_{16}$; is denser than naphtha, oily, and boils at 239°. The density of its vapour is by observation 4000, by calculation 3920. Naphtene thus forms, from its composition, the fourth member of the series of hydrocarbons to which olefiant gas belongs:

Methylene (hypothetical)	$C_2 H_2$
Olefiant gas . , .	$C_4 H_4$
Oil gas	$C_8 H_8$
Naphtene . . .	$C_{16} H_{16}$
Cetene	$C_{32} H_{32}$

Naphtol, $C_{24}H_{22}$; like naphtene, greatly resembles naphtha in its chemical properties, boils at 374°. The density of its vapour is by observation 5300, by calculation 5600. Naphtol and naphtene give compounds with chlorine, bromine and iodine.

It is evident from its composition that natural naphtha must be the product of the action upon vegetable matter of a high temperature, which has not however exceeded a red heat.*

CHAPTER IV.

AMYGDALIN AND THE BODIES DERIVED FROM ITS DECOMPOSITION.

SECTION I.

AMYGDALIN.

The formula of anhydrous amygdalin is $C_{40}H_{27}N O_{22}$.

This is a principle in the bitter almond and berries of the cherry-laurel, of which the discovery is due to Robiquet and Boutron-Charlard. Its singular decomposition and the nature and relations of the products resulting from it were ably investigated by MM. Liebig and Wœhler in a memoir, the publication of which formed an important era in the progress of organic chemistry (An. de Chim. li, 273.)

A fat oil is obtained by submitting blanched bitter almonds to great pressure between two hot iron plates; the matter which remains, or the almond cake, is the source of amygdalin. It is treated with boiling alcohol of 93 or 94 per cent applied to it in successive portions, and the alcoholic solutions evaporated by a water-bath to a syrupy consistence. To remove a quantity of sugar which prevents the amygdalin from crystallizing, the residue is diluted with water, a little yeast added to it, and it is left to ferment in a warm place. After the fermentation ceases, the liquid is filtered and evaporated again by a water-bath to a syrupy consistence. On mixing the syrup with a portion of strong alcohol of 94 per cent, all the amygdalin precipitates in the form of a white crystalline powder, which is pressed in folds of filter paper, and afterwards purified by new crystallizations from alcohol. (Liebig).

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* Journal de Pharmacie, t. 26, p. 549.

As crystallized from alcohol, amygdalin retains a portion of that substance in combination, which it loses when exposed to air. At the ordinary temperature it is scarcely soluble in anhydrous alcohol, but is more easily dissolved by boiling alcohol. It is very soluble in water, and crystallizes from a solution saturated at 104° in large transparent prisms, of a silky lustre which contain 10.57 per cent of water, or 6 atoms; dried in vacuo over sulphuric acid the crystals lose 3.52 per cent of water, equivalent to 2 atoms. The crystals are not volatile, but are decomposed by a high temperature, diffusing the odour of hawthorn, and leaving a bulky charcoal.

Dry chlorine has no effect upon amygdalin; humid chlorine converts it into a bulky white powder, insoluble in water and alcohol, which has not been examined. Heated with dilute nitric acid, or with peroxide of manganese and dilute sulphuric acid, amygdalin produces ammonia, volatile oil of bitter almonds, benzoic acid, formic and carbonic acids. Hypermanganate of potash in decomposing amygdalin gives rise to cyanate and benzoate of potash. Caustic alkalies convert amygdalin into ammonia, which is disengaged, and amygdalic acid, a peculiar acid, which remains in combination with the alkali.

AMYGDALIC ACID.

Formula: $HO+C_{40}H_{26}O_{24}$. This acid was first obtained by Liebig and Wœhler, by the action of alkalies upon amygdalin. It is best prepared by dissolving amygdalin in barytes-water, and maintaining the mixture in a state of ebullition, so long as ammonia is disengaged; the barytes is then removed by sulphuric acid, and the liquid evaporated by a water-bath. In the formation of this acid, 1 atom of amygdalin and 2 atoms of water are resolved into 1 atom of ammonia and 1 atom of anhydrous amygdalic acid:

$$C_{40}H_{27}NO_{22} \text{ and } 2\ HO = C_{40}H_{26}O_{24} \text{ and } NH_3.$$

Amygdalic acid is obtained by evaporation as a transparent colourless amorphous mass; it has a very agreeable acid taste, is insoluble in alcohol and ether, but so soluble in water as to deliquesce in damp air.

Nitric acid and the mixture of peroxide of manganese and dilute sulphuric acid act on amygdalic acid as on amygdalin, allowing for the absence of nitrogen from the former, the products being volatile oil of bitter almonds, formic and carbonic acids, all of which are disengaged in the state of gas.

Little is known of the amygdalates; they appear to be in general soluble salts, with the exception of a basic salt of lead. Amygdalin, it will be observed, has the composition of amygdalate of oxide of ammonium, from which the elements of 3 atoms of water have been abstracted; or it has lost 1 atom of water more than a true amygdalamide (Liebig).

SECTION II.

BENZOYL SERIES OF COMPOUNDS.

Benzoyl or *benzoïle*,* $C_{14}H_5O_2$=Bz. This is the hypothetical radical of a series of compounds, including benzoic acid, (from which it derives its name), and the essence or volatile oil of bitter almonds. The last substance is derived from amygdalin by various means. Amygdalin exists also in the kernels of many fruits, and in the leaves of the laurel.

BENZOIC ACID.

Formula: $HO,C_{14}H_5O_3$=HO, BzO. This acid exists ready formed in several resins, particularly benzoin and dragon's blood. It is produced by the decomposition of amygdalin by oxidating matters, by the oxidation of essence of bitter almonds, of hippuric acid, and in many other circumstances.

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* *Benzule* of several English chemical writers.

To prepare benzoic acid from the resin, Dr. Mohr directs 1 pound of it to be broken and spread uniformly in a cast iron bason, 8 or 9 inches in diameter and 2 inches deep, the mouth of which is then covered, like a drum, by unsized paper pasted down at the edges. A cylindrical vessel of paper of the size and ordinary form of a man's hat is pulled over this, and bound about the bason by a thread. The bason is then placed on a sand-bath for three or four hours, attention being paid to the management of the heat, for the beauty and purity of the product depend entirely upon the slowness and regularity with which the sublimation is effected. The paper cylinder is found completely filled with superb crystals of benzoic acid of splendid whiteness and perfectly free from the black empyreumatic oil which they are generally soiled with; but having on the contrary a strong and very agreeable odour of benzoin. This process yields about 4 per cent of benzoic acid.

Benzoic acid is also prepared in the humid way; the resin is finely pulverised and care taken to mix it intimately with an equal weight of hydrate of lime; the mixture is then boiled with twenty times its weight of water by which the benzoate of lime is dissolved; the solution is filtered, and after being concentrated to about one-fifth of its bulk hydrochloric acid is added, by which the benzoic acid is liberated, and crystallizes on cooling. The chief point to be attended to in this process is the mixing of the resin and hydrate of lime, which must be intimate, otherwise the mass agglomerates in boiling water, and the benzoic acid can only be obtained by reducing the mass to powder and mixing it again with hydrate of lime.

The benzoic acid may be purified by a second sublimation, or by sending a stream of chlorine through its solution in boiling water (Liebig's Traité.)

Benzoic acid crystallizes when sublimed in long hexagonal silky needles; when pure it is colourless and inodorous; but it acquires by heat an odour, analogous to that of benzoin. Its taste is sweet and hot, but quite peculiar. It reddens litmus feebly; water dissolves $\frac{1}{12}$ of its weight of benzoic acid at 212°, and $\frac{1}{200}$ only at the ordinary temperature. It is soluble in two parts of alcohol and the same quantity of ether, and dissolves also in oil of turpentine. Benzoic acid fuses at 248°, and sublimes at 293°, phosphorescing in the dark; it boils at 462°.2 (239°

centig.); the density of its vapour is 4270 by experiment, and 4260 by calculation. Heated in open air it allows a white vapour to diffuse, which greatly irritates the fauces and provokes coughing. It is very inflammable, and burns with a white smoky flame without leaving any residue.

Benzoates. Benzoic acid is readily dissolved by alkalies and alkaline carbonates, and also by phosphate of soda. Several insoluble benzoates are dissolved, according to Lecanu and Serbat, by acetates of potash and soda and nitrate of soda, while they are insoluble, in nitrate and sulphate of potash, and sulphate of soda. *Ammonia* forms a neutral and acid benzoate; the last presents itself in large regular crystals. The salts of *potash, soda, lithia,* and *magnesia* are very soluble, and crystallize with difficulty. The salt of *lime* is soluble in 20 parts of cold water, and in a greater proportion in boiling water; it crystallizes in flexible needles, or brilliant prisms, which contain 1 atom of water of crystallization. Benzoate of *alumina* is obtained as a crystalline precipitate. Benzoates of *manganese* and *protoxide of iron* are pretty soluble. Neutral benzoate of *peroxide of iron,* Fe_2O_3+3BzO, is soluble in water and alcohol and crystallizable. But peroxide of iron is thrown down in the form an insoluble sub-benzoate, of a reddish white or buff colour, when a soluble benzoate is added to a solution of peroxide of iron, previously neutralised without precipitating any peroxide of iron by means of ammonia. To prevent the decomposition of this precipitate and the formation of a soluble benzoate of iron, it should be washed by a solution of sal ammoniac. Benzoate of ammonia is often employed to separate peroxide of iron from oxides of manganese, nickel, and zinc, but when the solution contains at the same time alumina, yttria, zirconia, or glucina, the process does not answer, as the benzoates of these oxides are equally insoluble with that of peroxide of iron. Benzoate of *lead* is nearly insoluble in water, but soluble in acetic acid, from which it may be obtained crystallized in plates, which contain 2 atoms of water, one of which it abandons when dried at 212°. Solutions of an alkaline benzoate and trisacetate of lead, give a white anhydrous and insoluble precipitate, which is basic benzoate of lead consisting of 2 atoms of benzoic acid united with 3 atoms of oxide of lead. Benzoate of *silver* is obtained in colourless needles, flattened and brilliant, on treating a boiling and dilute solution of an alkaline benzoate with nitrate of silver, and allowing the liquid to cool.

HYDRURET OF BENZOYL, OR ESSENCE (VOLATILE OIL) OF BITTER ALMONDS.

Formula $C_{14}H_5O_2+H=Bz,H$. The crude oil obtained by distilling laurel leaves or bitter almonds with water, contains hydrocyanic acid, benzoic acid and some benzoine (a solid oil); it is purified by a new distillation with water, protochloride of iron and hydrate of lime in a thin liquid. The oil which distils over may be dried perfectly by digestion with chloride of calcium.

Pure hydruret of benzoyl is a transparent colourless liquid, of high refracting power; its odour is strong and peculiar having some resemblance to that of hydrocyanic acid, its taste burning. It is poisonous. The density of the oil is 1.043, its boiling point 356°; its vapour may be transmitted through a tube heated to redness without being decomposed. It inflames easily in air, and burns with a white smoky flame. It is soluble in 30 parts of water, and may be mingled in all proportions with alcohol and ether. Nitric acid dissolves hydruret of benzoyl, but converts it with difficulty into benzoic acid. Hydruret of benzoyl is gradually converted in air into benzoic acid by absorbing 2 atoms of oxygen, an atom of water being formed at the same time which combines with the benzoic acid formed. In presence of an alkali it absorbs oxygen rapidly and is transformed almost immediately into a benzoate. When mixed with dry hydrate of potash, and distilled at a high temperature out of contact with air, it forms benzoate of potash, by the decomposition of water, and pure hydrogen gas is disengaged. Submitted to a moderate heat with an alkali it gradually produces, according to Fremy, an alkaline benzoate and a volatile oily liquid very rich in hydrogen. Dilute solutions of the alkalies, barytes, or lime-water, dissolve hydruret of benzoyl, but do not alter it, even when kept for 24 hours at 140° or 160°, provided air is excluded. But all these solutions furnish a notable quantity of the solid benzoine, when after having added to them some drops of hydrocyanic acid they are exposed to a temperature of 158°. On treating hydruret of benzoyl with an alcoholic solution of potash, it passes in a few seconds into benzoate of potash which floats upon the alcohol; a portion of the hydruret of benzoyl which loses oxygen being converted at the same time into an oil of unknown composition retained in solution by the alcohol.

Chloride of benzoyl $C_{14}H_5O_2+Cl=Bz,Cl$; is formed on transmitting chlorine gas through dry hydruret of benzoyl, so long as hydrochloric acid is disengaged, and heating the yellow liquid to expel the excess of chlorine, till it becomes colourless. The atom of hydrogen of the hydruret of benzoyl is removed by one atom of chlorine, and replaced by another, as in ordinary substitutions.

Chloride of benzoyl is a colourless liquid, of a very penetrating and disagreeable odour, which affects the eyes; its density is 1.106; it boils at 383° (195° centig.). It may be distilled from lime or barytes without change. It mixes with ether and bisulphuret of carbon without decomposition. Cold water converts it more slowly than hot water into hydrochloric and benzoic acids; with alkalies it produces an alkaline benzoate and chloride of the same metal. With alcohol it produces benzoate of ether and hydrochloric acid.

Bromide and *iodide of benzoyl* crystallize in transparent colourless plates.

Sulphuret of benzoyl is obtained by distilling chloride of benzoyl with sulphuret of lead, as a yellow oil, which fixes as a soft crystalline mass, having a peculiar disagreeable odour.

Cyanide of benzoyl is prepared by distilling chloride of benzoyl with cyanide of potassium; it is, after rectification, a colourless oil having a strong cinnamon odour which excites tears.

Benzamide, $Bz+NH_2=Bz,Ad$; is prepared by saturating chloride of benzoyl by dry ammoniacal gas; pulverising the white solid mass which is formed, washing it with cold water to remove sal ammoniac, and dissolving the residue in boiling water, which deposits the benzamide on cooling. It crystallizes in right rhomboidal prisms, or in small tables of a pearly lustre, fuses at 239° into a colourless liquid, and may be distilled at a higher temperature. It is soluble in alcohol and ether, as well as in water. Acids and alkalies decompose it, with the presence of water, into ammonia and benzoic acid.

Formobenzoïlic acid, $HO + BzH,C_2HO_3$. This acid contains hydruret of benzoyl in combination with formic acid. It is the result of the action of dilute hydrochloric acid upon the crude distilled water of bitter almonds which contains the essence and hydrocyanic acid. The latter acid is decomposed in contact with water and a strong acid, into ammonia and formic acid, the last of which unites in the nascent state with the oil. This acid is a white crystalline powder, very acid, fusible into an oily liquid by heat with loss of water, soluble easily in water, alcohol and ether; capable of decomposing with aid of heat the acetates, carbonates and benzoates. Its aqueous solution when submitted to oxidating agencies, such as chlorine, nitric acid, and peroxide of manganese with dilute sulphuric acid, gives carbonic acid and hydruret of benzoyl.

Formobenzoïlic acid has the same saturating power as formic acid, and belongs to that class of acids into the constitution of which some foreign body enters without neutralising them. In the formation of its salts, the basic water of the formula above is replaced by a metallic oxide.

Benzoate of hydruret of benzoyl; a body which consists of 1 atom of hydrated benzoic acid united with 2 atoms of hydruret of benzoyl. It is prepared by saturating the crude essence of bitter almonds by humid gaseous chlorine; after some time the new compound is deposited in a crystalline mass, which is washed with cold ether. It forms either a crystalline powder of great whiteness, or slender short prisms of a square base, transparent and brilliant. It is soluble in alcohol, very slightly soluble in cold ether, and insoluble in water. It is decomposed immediately by an alcoholic solution of hydrate of potash, which deposits benzoate of potash after a time in regular crystals.

HIPPURIC ACID.

Formula: $HO + C_{18}H_8NO_5$.

This acid was discovered by Liebig, and obviously belongs to the benzoyl series, although its exact place cannot at present be assigned to it with certainty. It has been viewed as a compound of benzamide with an organic acid namely C_4HO_3 (aconitic, fumaric or equisetic acid); or as a compound of hydruret of benzoyl, hydrocyanic and formic acids. It exists in large quantity in the urine of herbivorous mammifers, and was first derived from that of the horse; hence its name.

To prepare it the fresh urine of the cow or horse is evaporated by a gentle heat, care being taken not to allow it to enter into ebullition; it is then made sharply acid by means of hydrochloric acid, and left to itself. The hippuric acid which crystallizes from this liquid is coloured and impure, but may be purified by adding a little hydrochloric acid to it with portions of chloride of lime till the odour and colour disappear.

Hippuric acid crystallizes in pretty large semi-transparent prisms of four sides and dihedral summits, which have a slightly bitter taste, and redden litmus strongly. They fuse by heat into an oily liquid without loss of weight; at a higher temperature the acid undergoes decomposition and is converted into benzoic acid and benzoate of ammonia, which distil over in red drops, diffusing an agreeable odour like that of the Tonquin bean, which is occasioned by an oily product of the reaction; while towards the end of the distillation hydrocyanic acid appears and a porous residue of charcoal. Cold water dissolves $\frac{1}{400}$ of hippuric acid, hot water dissolves it very abundantly; it is more soluble in alcohol, and very slightly soluble in ether.

Hydrochloric acid dissolves hippuric acid without decomposing it; nitric acid converts it almost immediately into benzoic acid. Peroxide of manganese and sulphuric acid convert it, with the aid of heat, into carbonic acid, ammonia and benzoic acid. Boiled with puce coloured oxide of lead, hippuric acid is converted into benzamide and carbonic acid.

After the urine of the horse is left to itself for a long time, or evaporated rapidly, it contains benzoic acid and no hippuric acid. M. Liebig expresses an opinion that hippuric acid is not a product of the animal economy, but comes from the food of the animals, in which it may exist ready formed. For it is observed that the urine of horses living on green food, always furnishes hippuric acid, while the urine of animals fed on dry herbs or hay, which has undergone a kind of fermentation, contains only benzoic acid. Mr. Alexander Ure has since made the curious observation that benzoic acid taken internally by man is discharged in the urine as hippuric acid, while the proportion of uric acid in the urine suffers at the same time a great diminution or is reduced to nothing.*

The *hippurates* of the alkalies and alkaline earths are soluble and crystallizable. Those of the metals proper with the exception of iron are very sparingly soluble in cold, but more soluble in hot water and crystallize on cooling. The stronger acids separate hippuric acid from all the hippurates; distilled with lime or hydrate of potash they give ammonia with an oily liquid supposed to be benzin.

PRODUCTS OF THE DECOMPOSITION OF BENZOYL COMPOUNDS.

Hyposulphobenzoic acid, $2HO + C_{14}H_4O_3,S_2O_5$; a bibasic acid discovered by Mitscherlich. It is prepared by conducting the vapour of anhydrous sulphuric acid into a dry receiver containing benzoic acid and surrounded by cold water; a viscid mass is formed like turpentine, which is taken up by water, and after the uncombined benzoic acid has subsided from the liquid, the latter is neutralised with carbonate of barytes, and after evaporating the mixture, some hydrochloric acid is added to it; the acid hyposulphobenzoate of barytes crystallizes upon cooling. The free acid is obtained by precipitating the barytes of the last salt by sulphuric acid, filtering, evaporating the solution by the naked fire and finally in vacuo over sulphuric acid; in this way the acid is obtained in a crystalline state. The crystals may be heated to 302° without alteration, but at a higher temperature they are decomposed.

This acid forms both an acid and neutral class of salts, the first containing one atom of water and one atom of metallic oxide as base, the other two atoms of metallic oxide. All these salts when distilled with an excess of hydrate of potash leave a residue composed of sulphate and sulphite with carbonate of potash, indicating the presence of hyposulphuric acid in the original compound. *Acid hyposulphobenzoate of barytes* crystallizes in oblique rhomboidal prisms, soluble in 20 parts of cold water, and containing 9.6 per cent of water of crystallization or 3 atoms, which it loses at 212°.

Neutral hyposulphobenzoate of barytes, $2BaO + C_{14}H_4O_3, S_2O_5$; is obtained by boiling the acid salt with carbonate of barytes;

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* Proceedings of the Pharmaceutical Meetings at Mr. Bell's, Part 1, vol. I. 1841.

it is more soluble than the former salt, but crystallizes with difficulty in a regular form. It will be observed that hyposulphobenzoic acid is formed by the abstraction of the elements of 1 atom of water from 1 atom of benzoic acid and 2 atoms sulphuric acid, and that it retains the saturating power of 2 atoms of acid, being bibasic.

Nitrobenzoic or benzoënitric acid, $HO+C_{14}H_4O_3, NO_4$; an acid formed by the abstraction of HO from the elements of nitric acid and benzoyl. It is prepared by boiling benzoic acid with an excess of nitric acid, the first is dissolved and colours the fluid red; deutoxide of nitrogen is evolved as an accidental product arising from the action of the nitric acid on the nitrobenzoic acid already formed. From the cold solution crystals similar to benzoic acid are deposited; the fluid eventually becomes a solid crystalline mass. At 50°, 400 parts of water dissolve 1 part of the acid, at 212° 10 parts. It dissolves easily in alcohol and ether; fuses at 260°.6 (127° centig.), but begins to sublime at 230°; the pure acid sublimes unchanged; chlorine has no action upon it.

The *nitrobenzoates* are for the most part soluble in water and alcohol, crystallizable, explode by heating, and when gently warmed give off nitrobenzide ($C_{12}H_5NO_4$). *Ammonia* forms a neutral and acid salt. The salt of *lime* is acicular and contains 2 atoms of water, which are driven off at 374°. The salt of *barytes* loses 4 atoms of water at 212°. The salt of *strontian* loses 2½ equivalents of water at 266°. When acid nitrobenzoate of ammonia is added to a solution of sulphate of zinc, a gelatinous basic salt precipitates, containing 4 atoms of *oxide of zinc* to 1 atom of acid. The filtered solution gives the neutral salt of zinc in crystalline plates, which contain 5 atoms of water. The salt of *copper* is a blue powder soluble in hot water, containing 1 atom of water. Besides a neutral nitrobenzoate of *lead*, a remarkable sub-salt exists, in which 1 atom of oxide of lead is united with 5 atoms of the neutral salt. Nitrobenzoic acid forms fine crystallizable compounds with both oxide of ethyl and oxide of methyl. (Mulder, Mitscherlich.)

Bromobenzoic acid, $2HO+C_{28}H_9BrO_8$; a bibasic acid, discovered by Peligot, and formed by the action of 4 atoms of bromine upon 2 atoms of benzoate of silver:

$$C_{28}H_{10}O_8+2Ag \text{ and } 4Br=C_{28}H_9BrO_8 \text{ and } 2AgBr \text{ and } HBr.$$

When bromobenzoic acid is precipitated from its salts by a strong acid, the latter assumes the two atoms of water of the bromobenzoic acid, which is thrown down anhydrous. The bromobenzoates are in general crystallizable salts, that of the peroxide of iron is insoluble, and has the properties and appearance of the benzoate of iron.

BENZOLE.

Syn. *Benzin, benzene, phene.* Formula $C_{12}H_6$.

This compound, which is named benzole by Liebig, the termination *ole* being assigned to hydrocarbons, was originally obtained by Mr. Faraday from the condensed liquid of compressed oil gas and described under the name of bicarburet of hydrogen; more lately Mitscherlich found that it was the principal product formed on distilling benzoic acid with hydrate of lime, and named it benzin. By the abstraction of the elements of 2 atoms of carbonic acid from 1 atom of crystallized benzoic acid:

$$C_{14}H_6O_4—C_2O_4 \quad C_{12}H_6.$$

Benzole is prepared by distilling 1 part of crystallized benzoic acid with 3 parts of hydrate of lime; rectifying the oily product by a second distillation with water, or better from quicklime. It is a limpid colourless liquid, of a peculiar ethereal odour which is agreeable; its density is 0.85; it boils at 186°.8 (86° centig.); the density of its vapour is 2378, its combining measure 4 volumes; at 32° it becomes a crystalline mass, which becomes liquid at 44°.6 (7° centig.) Benzole, is insoluble in water, soluble in alcohol and ether. It is not decomposed by any hydrated acid.

Sulphobenzide, $C_{12}H_5SO_2$ (Mitscherlich). Benzole like naphtaline affords several products when decomposed by acids. When exposed to the vapour of anhydrous sulphuric acid it forms a viscid liquid, which dissolves entirely in a small quantity of water; on adding a larger quantity of water, sulphobenzide falls as a precipitate, which, dissolved in ether, gives sulphobenzide crystallized, by evaporation. Sulphobenzide is a colourless substance, perfectly neutral; it fuses at 212°, boils at a higher temperature and sublimes unchanged. In the formation of this substance 1 atom of anhydrous sulphuric acid and 1 atom of benzole abandon 1 atom of water:

$$C_{12}H_6 \text{ and } SO_3 = C_{12}H_5SO_2 \text{ and } HO.$$

Hyposulphobenzidic acid, sulphobenzinic acid, benzosulphuric acid, HO, $C_{12}H_5S_2O_5$; this acid remains in the liquid which deposits sulphobenzide. It is also produced on dissolving benzole in oil of vitriol, or in fuming sulphuric acid. It is a very acid liquid, which crystallizes, and resists a temperature of 392°. It may be viewed as a compound of sulphobenzin with hydrated sulphuric acid. *Hyposulphobenzidate of copper* forms large regular crystals. (Mitscherlich).

Nitrobenzide, $C_{12}H_5NO_4$, a liquid compound obtained by dissolving benzole to saturation in hot concentrated nitric acid; on diluting the acid with water and allowing it to cool, the liquid separates and subsides to the bottom. At 59° nitrobenzide is yellow, has a sweet taste and the odour of cinnamon. Its density is 1.209, that of its vapour 4294; it boils at 433.°4 (223° centig.), crystallizes in needles at 37°.4 (3° centig.). It is insoluble in water, soluble in alcohol and ether; dilute acids also dissolve it; alkalies do not decompose it. (Mitscherlich).

Azobenzide, $C_{12}H_5N$, a volatile, red, crystalline substance, obtained on distilling an alcoholic solution of nitrobenzide with dry hydrate of potash. It is fusible at 149°, and boils at 379°.4 (193° centig.).

Chloride of benzole, $C_{12}H_6Cl_6$, a crystalline substance, obtained on exposing benzole to chlorine gas, in sunshine; 6 atoms of chlorine unite with the benzole without displacing any hydrogen. (Mitscherlich).

Chlorobenzide, $C_{12}H_3Cl_3$, an oily liquid, obtained by distilling chloride of benzole from hydrate of lime. It boils at 410°, its density is 1.157, that of its vapour 6370.

Bromine forms analogous compounds with benzole.

Benzone, $C_{13}H_5O$, one of the liquid products of the distillation of crystallized benzoate of lime:

1 at. of benzone . . .	$C_{13}H_{10}O$
1 at. of carbonic acid .	$C \quad O_2$
1 at. of lime	$CaO.$
1 at. of benzoate of lime	$C_{14}H_5 O_3 + CaO.$

The crude product of the distillation contains also benzole and naphtaline, of the first of which it is divested by heating it on a water-bath, and keeping it for a sufficient time at 392°, and of the second by exposing the liquid thus obtained to a cold of —4°, when naphtaline separates. Benzone is oily and viscid; not altered by nitric acid and hydrate of potash, but decomposed by chlorine and sulphuric acid. (Peligot).

PRODUCTS OF THE DECOMPOSITION OF HYDRURET OF BENZOYL.

Hydrobenzamide, $C_{42}H_{18}N_2$, or $C_{14}H_6N_{\frac{2}{3}}$. Hydruret of benzoyl is acted upon when mixed with twenty times its volume of a concentrated solution of ammonia in a vessel hermetically sealed, and kept for several hours at a temperature of 104° to 122° (40 to 50° centig.). A crystalline mass of hydrobenzamide is formed, which may be purified from the oil by washing with cold ether, in which hydrobenzamide is insoluble, dissolving the residue in alcohol, and evaporating at the usual temperature, when hydrobenzamide is obtained in regular crystals. They are colourless octohedrons or rhomboidal prisms, which enter into fusion at 230°, and are decomposed by dry distillation leaving a residue of charcoal. The alcoholic solution is converted by boiling into ammonia and hydruret of benzoyl. This substance is formed by the abstraction of the elements of 6 atoms of water from 3 atoms of hydruret of benzoyl and 2 atoms of ammonia (Laurent):

$$3\ (C_{14}H_6O_2) \text{ and } 2NH_3 = C_{42}H_{18}N_2 \text{ and } 6HO.$$

The whole oxygen of the oil and whole hydrogen of the ammonia separate as water; the formation of this substance is, therefore, different from that of an ordinary amide. It is, indeed, simply a hydruret of benzoyl, in which the 2 atoms of oxygen are replaced by $N_{\frac{2}{3}}$.

Benzhydramide, a crystalline substance, isomeric with hydrobenzamide. *Azobenzoïle*, $C_{42}H_{15}N_2$, or $C_{14}H_5N_{\frac{2}{3}}$; a white crystalline powder, soluble in alcohol. *Benzoilic azotide*, $C_{14}H_5N$, a white, insipid, crystalline powder, insoluble in boiling alcohol. These three bodies were derived by Laurent from a yellow resinous mass, which is formed by the action of solution of ammonia, upon the crude essence of bitter almonds of commerce.

Hydruret of sulphobenzoyl, $C_{14}H_5S_2+H$; a body representing the hydruret of benzoyl, of which the 2 atoms of oxygen of the benzoyl are replaced by 2 atoms of sulphur. M. Laurent has generally succeeded in preparing this compound by dissolving 1 volume of the crude essence of bitter almonds in 8 or 10 volumes of alcohol, and then adding gradually 1 volume of sulphuret of ammonium. The liquor becomes turbid in a few minutes, and allows a white powder to fall, similar to farina. By throwing this on a filter, and washing it several times with boiling alcohol, the hydruret of sulphobenzoyl is usually obtained pure. It is white, pulverulent, and composed of small rounded grains, like those of starch, without a trace of crystallization. Although apparently inodorous, it communicates a highly disagreeable odour to the hands. It is insoluble in water and alcohol, slightly soluble in ether. It is slowly decomposed by an alcoholic solution of potash.[*]

Hydruret of sulphazobenzoyl, a crystalline compound, formed by dissolving essence of bitter almonds in 4 or 5 volumes of ether, adding to it 1 volume of sulphuret of ammonium, and leaving the whole for fifteen days or a month. It forms a white crystalline crust, which it is necessary to dissolve and crystallize from ether to purify it. Its analysis represents a compound of 6 atoms of hydruret of sulphobenzoyl with 1 atom of hydrobenzamide:

$$6\,(C_{14}H_5S_2+H)\ +C_{42}H_{18}N_2.$$

Other views may be taken of the constitution of this substance. On the theory upon which it is named by Laurent, it is benzoyl in which the 2 equivalents of oxygen are replaced by 2 equivalents made up of sulphur and nitrogen:

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[*] Sur de Nouvelles combinaisons benzoïliques azotées et sulphurées; par M. Laurent.—Annales de Chimie, &c. 3me Série, tome 1, p. 292.

$$C_{14}H_5S_{\frac{4}{3}}N_{\frac{2}{9}}+H.$$

Or, multiplying the preceding formula by three, as 2 atoms of hydruret of sulphobenzoyl, and 1 atom of hydruret of azobenzoyl:

$$2\,(C_{14}H_5S_2+H)+(C_{14}H_5N_{\frac{2}{3}}+H).$$

In these formula, $N_{\frac{1}{3}}$ is made equivalent to S or O, an opinion which M. Laurent has long maintained.

Benzimide, $C_{28}H_{11}NO_4$, a substance discovered by Laurent in crude essence of bitter almonds. It crystallizes in white needles, which have a pearly lustre and are very light.

ISOMERIC COMPOUNDS OF BENZOYL.

Benzoïne, $C_{14}H_6O_2$, a crystalline substance, having the same composition as hydruret of benzoyl, into which the latter is often converted in a manner that is not understood. It is never produced in the pure hydruret of benzoyl, but is formed in the essence, which contains hydrocyanic acid, by the presence of alkalies, sulphuret of sodium and cyanide of potassium. The essence may be converted entirely into benzoine, by mixing it with an equal volume of a solution of potash in alcohol kept cold. It is purified by repeated crystallizations from alcohol.

Benzoïne crystallizes in colourless prisms of high lustre, is inodorous, tasteless, fuses at 248°, and distils at a higher temperature without being modified. It is slightly soluble in hot water, but insoluble in cold, more soluble in hot than cold alcohol.

Hydrobenzoïnamide, a white powder, obtained by treating benzoïne with solution of ammonia at a gentle heat, isomeric with hydrobenzamide (Laurent).

Benzile, $C_{14}H_5O_2$, a substance which crystallizes in regular six-sided prisms, of a rhombic base, and sulphur-yellow colour; formed by passing a stream of chlorine gas through fused benzoïne, so long as hydrochloric acid is disengaged. It is inodorous, tasteless, fuses between 194 and 197° (90 and 92° cent.). May be distilled, or dissolved in concentrated sulphuric acid without change. The aqueous solution of potash has no effect upon it, but the alcoholic solution converts it into benzilic acid (Laurent).

Benzilic acid, $HO + C_{28}H_{11}O_5$; may be separated from benzilate of potash by an excess of hydrochloric acid. The acid crystallizes on cooling, in colourless rhombohedrons, of high lustre, or in long prismatic needles. It fuses at 248°, and is decomposed at a higher temperature, giving a sublimate of benzoic acid, accompanied by violet vapours, and a residue of carbon. It forms a lively crimson solution in cold oil of vitriol. Benzilic acid contains the elements of 2 atoms of benzile and 2 atoms of water, one of which remains basic to the acid, and is replaced in the benzilates by a metallic oxide. *Benzilate of potash* forms large limpid crystals, soluble in water and alcohol. (Liebig).

Azobenzoïde, $C_{42}H_{16\frac{1}{2}}N_{2\frac{1}{2}}$; a white pulverulent substance, described by Laurent, but of which the composition is rather doubtful.

Cyanobenzile, a substance which is deposited in transparent, voluminous crystals, when to an alcoholic solution of benzile, one third of its bulk of very concentrated hydrocyanic acid is added, and the whole gently heated. (Von Zinin).

SYNAPTASE.

The white of both sweet and bitter almonds consists, in a great measure, of a peculiar matter, very soluble in water, which was named synaptase by M. Robiquet. To prepare it, he directed sweet almonds, from which all the fat oil has been expressed, to be mixed intimately with twice their weight of water, allowed to macerate thus for two hours, and then to be submitted to pressure, which is uniformly increased. The filtered liquid contains vegetable albumen, which is thrown down by acetic acid, and gum, which is precipitated by acetate of lead. A liquid remains, which contains some free acetic acid, acetate of lead, sugar and synaptase; the lead is thrown down by sulphuretted hydrogen, and the synaptase by alcohol, while the free acid and sugar remain in solution. The precipitated synaptase is washed with alcohol, and dried in vacuo over sulphuric acid.

Dry synaptase is described as a yellowish white, opaque, horny mass, hard and friable ; very soluble in cold water. In a fresh solution, iodine produces a deep rose colour, without any precipitate. The solution of synaptase does not keep, but soon becomes turbid from the formation of a white precipitate, and acquires a mouldy ódour. It is precipitated from solution by alcohol, in flocks, which redissolve in an excess of water. Acids do not produce a precipitate in its solution; at 140° it coagulates like albumen. It contains azote, and produces ammonia and a new acid in boiling solutions of the alkalies. The composition of synaptase has not been determined.

A matter which, if a pure substance, is probably the same was obtained by Liebig and Wœhler, and named *emulsin*, by treating an emulsion of sweet almonds with ether, to take up all the fat oil, and then precipitating the transparent, syrupy liquid which remained, by alcohol, a white matter was abundantly thrown down, which formed, when dry, a horny, semi-transparent mass. This substance gives much ammonia when boiled with a solution of barytes or a caustic alkali. There are no means of determining the atomic composition of emulsin, but the following are the results of two analyses of it by Dr. R. D. Thomson and Mr. Richardson :

Carbon . . .	49.025	48.555
Hydrogen . . .	7.788	7.677
Oxygen . . .	24.277	25.026
Nitrogen . . .	18.910	18.742
	100.000	100.000

The reaction which occurs when synaptase and the amygdalin of bitter almonds meet each other in solution is very remarkable, and a knowledge of it necessary to enable us to form a conception of the phenomena of the distillation of the bitter almond. I shall state here the latest view of it which has been taken by M. Liebig. On mixing a solution of 10 parts of amygdalin in 100 parts of water, with a solution of 1 part of synaptase in 10 parts of water, a particular decomposition immediately takes place; the mixture becomes opalescent without losing its transparency; acquires the odour of bitter almonds, and gives on distillation hydrocyanic acid and hydruret of benzoyl with the vapour of water. The residue is rendered turbid by coagulated synaptase, and on continuing the evaporation, a very sweet liquid is obtained, which contains crystallizable sugar. After destroying the sugar by fermentation, a fixed acid remains in the residue. The quantity of sugar obtained is more considerable than what the elements of the amygdalin could produce; it would appear, therefore, that the elements of the synaptase contribute to its formation. The decomposition is not complete unless the amygdalin and synaptase are dissolved in a proper quantity of water; if it is insufficient to dissolve the hydruret of benzoyl liberated, a corresponding quantity of amygdalin remains undecomposed. (Traité, p. 276).

The constituents of the bitter almond are the fixed oil, which is separated by expression, and the synaptase and amygdalin, the two last in such a condition that they cannot re-act upon each other. When the almond cake is treated with boiling alcohol, the amygdalin is dissolved out, and the synaptase coagulated. When the cake is moistened with water, the odour of hydrocyanic acid, and of the essence are immediately perceived, but the cake must be diffused through a certain quantity of water, in order that the mutual action of the synaptase and amygdalin may be complete, and that the whole of the last may disappear. In preparing the *distilled water of bitter almonds* of pharmacy, M. Liebig recommends that a mixture of 1 part of the cake and 20 parts of luke-warm water be made, and left to itself for twenty-four hours before submitting it to distillation.

One atom of amygdalin contains the elements of (Liebig):

1 equiv. of hydrocyanic acid . .	C_2	H	N	
2 equiv. of hydruret of benzoyl .	C_{28}	H_{12}		O_4
½ equiv. of sugar	C_6	H_5		O_5
2 equiv. of formic acid	C_4	H_2		O_6
7 equiv. of water		H_7		O_7
1 equiv. of amygdalin	C_{40}	H_{27}	N	O_{42}

One hundred parts of amygdalin are said to yield 47 parts of the crude essence of bitter almonds, and these 47 parts to contain 5.9 parts of free hydrocyanic acid. The last acid is not indicated by nitrate of silver added to a solution of the crude essence in water, owing to the presence of the oil; to obtain a precipitate of cyanide of silver, ammonia-nitrate of silver must be used, and the ammonia saturated with nitric acid, after the lapse of some time.

Laurel-water is prepared by distilling with water 2 parts of fresh leaves of the prunus laurocerasus, of which the three first portions are received; the product contains the same elements as the water of bitter almonds. The leaves contain amygdalin and another substance, which appears to act upon it when distilled with water, in a manner analogous to synaptase.

CHAPTER V.

ESSENCE OF CINNAMON AND BODIES DERIVED FROM IT.

CINNAMYL SERIES OF COMPOUNDS.

Cinnamyl, $C_{18}H_7O_2$=Ci; the hypothetical radical of the essence of cinnamon and of cinnamic acid.

Essence or oil of cinnamon.—According to the recent determinations of M. Mulder, $C_{20}H_{11}O$ is the formula for oil of cinnamon derived from the cinnamon of Ceylon, of Java and China, and of the flowers or bark of the cassia-tree. This essence absorbs oxygen from the air, and[*] forms cinnamic acid, two different resins and a new oil $C_{18}H_8O_2$, which appears to be the substance examined, and considered as oil of cinnamon by MM. Dumas and Peligot. The two resins have the composition $C_{30}H_{15}O_4$ and $C_{24}H_{10}O_2$.

This oil is obtained by distilling with water the bark of the *Laurus cinnamoneum*, or the flowers and bark of the cassia. It is yellow, becoming brown in air, with the odour of cinnamon, and a sweet and burning taste, its density 1.008 at 77°, boiling point 428°; it becomes solid at 23°. It is slightly soluble in water, and the solution produces with iodine and iodide of potassium, reddish brown crystals, of a metallic lustre, containing, according to Dr. Apjohn, KI+6 (CiH, I). The oil dissolves completely in potash, and affords on distillation an oil, lighter than water $C_{18}H_{10}O_2$, while the residue contains cinnamate of potash, and a black matter (Mulder). The bleaching chlorides convert essence of cinnamon into benzoic acid.

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[*] Journal de Pharmacie, t. 26, p. 549.

Cinnamic acid, $HO+C_{18}H_7O_3=HO+CiO$. This acid is formed by the oxidation of the essence of cinnamon in air, or by dissolving the oil of the balsam of Peru in an alcoholic solution of potash, evaporating to dryness, dissolving the residue of cinnamate of potash in boiling water, and liberating the cinnamic acid by an excess of hydrochloric acid. The cinnamic acid crystallizes on cooling in tufts of crystals, which are colourless, and have an aromatic and very acrid taste. The crystals fuse at 264°.2 (129° centig.) enter into ebullition at 554°, and distil over as a heavy oil, which fixes on cooling; they sublime at a lower temperature. Cinnamic acid is less soluble, both in cold and hot water, than benzoic acid, which it considerably resembles; very soluble in alcohol and ether; from alcohol it crystallizes in large rhomboidal prisms, which are hard and very friable. It may be distinguished from benzoic acid by nitric acid, which converts it into hydruret of benzoyl and nitrocinnamic acid; cinnamic acid also does not combine with sulphuric acid as benzoic acid does. The salts of cinnamic acid are monobasic, and have a great analogy to the benzoates. (Dumas and Peligot, Mulder).

Nitro-cinnamic acid, $HO+C_{18}H_6O_3, NO_4$; produced by the abstraction of HO from the elements of cinnamic acid and nitric acid. This acid is prepared by adding cinnamic acid in powder to strong nitric acid, preventing the temperature from rising above 140°. The cinnamic acid is at first dissolved; the mixture soon becomes hot, and a crystalline substance separates; the latter is washed with water, dissolved and crystallized from alcohol. Nitrocinnamic acid is white with a shade of yellow, fuses at 518°; heated above that temperature, it boils and is decomposed. This acid is almost insoluble in boiling water; it is also but sparingly soluble in alcohol, requiring 327 parts of alcohol to dissolve it at 68°, while cinnamic acid is soluble in 4.2 parts, benzoic acid in 1.96, and nitrobenzoic acid in somewhat less than its own weight.

The alkaline *nitrocinnamates* dissolve easily in water; the other salts are either soluble with difficulty or entirely insoluble; they explode when heated. The *ether* of this acid is formed by heating the latter with 20 parts of alcohol and a little sulphuric acid for several hours, at a temperature not exceeding 176°. The acid is dissolved, and the liquid on cooling deposits the nitrocinnamate of oxide of ethyl in prismatic crystals. This ether melts at 276°.8 (136° centig.), and boils at 572° but is then partly decomposed; it is not decomposed by ammonia.

When more than 1 part of cinnamic acid is added to 8 parts of nitric acid, the temperature rises above 140°, and nitrobenzoic acid is formed, with another acid not yet examined. (Mitscherlich.)

Hydruret of cinnamyl, $C_{18}H_8O_2=HCi$; an oily liquid obtained on adding water to the nitrate of hydruret of cinnamyl; discovered by Dumas and Peligot.

Nitrate of hydruret of cinnamyl, $C_{18}H_8O_2+HO,NO_5$; a compound formed on treating the essence of cinnamon of China, with concentrated and colourless nitric acid. The crystals first obtained are purified by pressure in paper, and afterwards crystallized from alcohol; it forms long oblique rhomboidal prisms, perfectly pure and colourless. This compound soon alters by keeping, disengaging nitrous acid and the hydruret of benzoyl; this decomposition is hastened by heating the compound slightly.

Chlorocinnose, $C_{18}H_4Cl_4O_2$.—This name is given by Dumas and Peligot to a chlorinated product of the essence of cinnamon. It is a volatile solid compound, crystalline and colourless at the usual temperature, which enters into fusion at a moderate heat and sublimes without residue. It is neither altered by concentrated sulphuric acid nor by gaseous ammonia.

Oil of the balsam of Peru.—This oil is obtained by treating 2 volumes of the balsam with 3 volumes of a solution of caustic potash of density 1.3, and floats over a dark watery fluid (Stoltz and Wernher). It is purified by distillation. This oil is termed *cinnameine* by M. Fremy. When boiled with an alkali it is transformed into cinnamic acid, and an indifferent substance to which Fremy has applied the name *peruvine*. This last is an oily colourless liquid lighter than water; its composition is expressed by $C_{18}H_{12}O_2$. Fremy finds the *balsam of Tolu* to contain the same bodies as the balsam of Peru. According to Richter the balsam of Peru contains two different oils, one of which is soluble in alcohol of 75 per cent and is called by him *myriospermine*, the other oil which is insoluble he names *myroxiline*. On treating the first with an alcoholic solution of potash, an acid is formed different in its capacity of saturation, according to Richter, from cinnamic acid, and which he names *myriospermic acid*. Its atomic weight deduced from the salt of silver is 1553.85.

CHAPTER VI.

SALICIN AND BODIES OBTAINED FROM ITS DECOMPOSITION.

SECTION I.

SALICIN.

Formula: $C_{42}H_{29}O_{22}=C_{42}H_{23}O_{16}+6HO$? (Mulder).

This neutral crystallizable substance was discovered by Buchner and Leroux in the bark of the *Salix helix*. It is contained in the bark and leaves of all the species of willow which have a bitter taste, and in some poplars. To prepare salicin the fresh bark or dry ground bark is boiled with water till a strong decoction is made; to the concentrated and boiling decoction oxide of lead is gradually added till the liquid is colourless. Gum, tannin and all extractive matters which may interfere with the crystallization of the salicin are thus carried down by the oxide of lead. The oxide of lead dissolved is then removed first by means of sulphuric acid, and then by sulphuret of barium. The liquid is crystallized by evaporation and the salicin made perfectly white by the use of charcoal and repeated crystallizations. The sulphuret of lead which is precipitated in the process also assists as a decolorising agent. The barks which contain much salicin yield it at once in crystals, when they are exhausted by cold water and the extract evaporated with caution, according to Merck.

Salicin crystallizes in delicate colourless needles of a silky lustre, which have a bitter taste, and no action on vegetable colours. It is persistent in air, loses nothing at 212°, fuses at 248°, and is decomposed by a higher temperature. Salicin is soluble in 5 or 6 times its weight of cold water, in much less boiling water, is very soluble in alcohol, but insoluble in ether and oil of turpentine. It dissolves purple red in concentrated sulphuric acid, a property by which it may be recognised even in the dry bark, the latter being stained red by sulphuric acid when it contains salicin.

Salicin does not combine with acids, nor possess alkaline properties. It is thrown down by the ammoniacal acetate of lead as a white precipitate, in which according to Piria 6 atoms of water belonging to salicin are replaced by 6 atoms of oxide of lead; but according to Ettling, the quantity of oxide of lead is not constant but increases with the washings to which the precipitate is submitted.

Saliretin, $C_{30}H_{15}O_7+HO$.—When raised to the boiling point with dilute sulphuric or hydrochloric acid, the solution of salicin soon becomes turbid, and allows a yellowish substance to fall having the consistence of a resin, which is saliretin. When prepared with concentrated acids, the product wants the atom of water represented in the formula, or is anhydrous. In this decomposition 1 atom of hydrated salicin is resolved into 1 atom of saliretin and 1 atom of grape sugar, which last is found in solution.

Saliretin is insoluble in water, and precipitated by that liquid from its solution in alcohol, in ether or concentrated acetic acid, in all of which it is very soluble. It is not soluble in ammonia, but is dissolved by the fixed alkalies and precipitated from them by acids. Saliretin is coloured blood-red by concentrated sulphuric acid; by nitric acid it is converted into carbazotic acid. (Piria).

Chorinated salicin, chlorosalicin.—Two compounds have been obtained by treating a solution of salicin by chlorine, one a crystalline yellow powder, $C_{42}H_{25}Cl_4O_{22}$, produced at the ordinary temperature; the other formed about 140°, a red oily liquid, $C_{42}H_{18}Cl_7O_{18}$.

Rutilin.—This name is applied by Braconnot to the product of the decomposition of salicin by sulphuric acid. Alkalies change its tint to a deep purple.

SECTION II.

SALICYL SERIES OF COMPOUNDS.

Salicyl, $C_{14}H_5O_4$=Sa; the hypothetical radical of salicylous acid, salicylic acid and some other compounds: equivalent to benzoyl plus 2 atoms of oxygen.*

Salicylous acid, spiroïlhydric acid, $H+C_{14}H_5O_4$=H,Sa. This substance was obtained by M. Piria by distilling salicin with dilute sulphuric acid and bichromate of potash, and has been shewn by Dumas and by Ettling to be the principal constituent of the oil obtained by Pagenstecher by distilling the flowers of the Queen of the meadow (*spiræa ulmaria*), and which M. Lœwig had analysed and described under the name of spiroilhydric acid.

The proportions lately recommended by Dr. Ettling for preparing salicylous acid from salicin are:

3	parts of salicin
3	parts of bichromate of potash
4½	parts of concentrated sulphuric acid
36	parts of water.

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* The name salicyl was applied by Dumas and Piria to this hypothetical radical, which was viewed as a higher degree of oxidation of benzoyl. The oil of spiræa ulmaria, or salicylous acid, is represented as the hydruret of this radical, which also exists in combination with potassium, &c., in the salicylites. An objection to and source of some confusion attending this view is that it represents salicyl as a salt radical or halogen body, combining directly with metals, and not as a basyle, like benzoyl, ethyl, and the other radicals with which it is associated.

M. Liebig points to an explanation of the isomerism of salicylous and benzoic acids and their salts, in the circumstance that while benzoic acid is monobasic, salicylous acid may have its equivalent multiplied by 2 or by 3, and be a bibasic or a tribasic acid. This supposition, however is not supported by the density

The bichromate of potash and salicin are intimately mixed, and after pouring over them two thirds of the water, the whole being well agitated in the retort, we add all at once the sulphuric acid previously diluted with the remaining third of the water, and agitate again. A feeble reaction slowly manifests itself, accompanied by a slight disengagement of gas, which lasts about half an hour or perhaps three quarters of an hour, when an ounce is employed for each part ordered; at the same time the liquid assumes an emerald tint and becomes warm. As soon as that reaction has ceased, the retort is placed upon the fire and moderately heated. The water vapour carries over the salicylous acid, which separates after some time. It is purified by washing it with water and rectifying from chloride of calcium. From half a pound of salicin Dr. Ettling obtained two ounces of the oil.*

Salicylous acid is an oily inflammable liquid, colourless or slightly yellow, having a burning taste, and agreeable aromatic odour; of density 1.1731, becoming solid at —4° (Lœwig); it boils at 385°.7 (196°.5 centig.) when prepared from salicin (Piria), while the oil from the flowers of the Spiræa boils at 359°.6 (182° centig.), according to Ettling. The density of its vapour is by observation 4276; by calculation 4260, or the same as that of benzoic acid. It dissolves easily in water, and may be mixed with alcohol and ether in all proportions; its solution in water reddens tincture of litmus, and discolours it after the lapse of some time. It is decomposed by sulphuric acid; also by chlorine, one atom of hydrochloric acid being formed and eliminated, and one atom of chlorine substituted for the hydrogen, as usual. When heated with an excess of hydrate of potash, salicylous acid is converted into salicylate of potash, with an escape of hydrogen gas. Potassium also when slightly heated in it, gives the same products.

Salicylous acid is recognised by producing a violet colour with salts of peroxide of iron, which disappears after some time. In the *salicylites*, the atom of hydrogen of the formula of salicylous acid is replaced by a metal. The salts of the fixed alkalies

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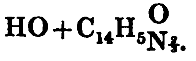
of salicylous acid in the state of vapour, which is the same as that of benzoic acid.

* Liebig's Annalen xxxv, 241; or Annales de Chimie, &c., 3me Série, t. 1, p. 490.

and ammonia are described as soluble and possessing an alkaline reaction, all the others as insoluble; most of them as yellow and containing water of crystallization. The salts of *lead* and *copper* are anhydrous. The neutral salt of *soda* contains 2 atoms of water which it loses at 248°, the salt of *barytes* contains 2 atoms of water. They are all decomposed by strong acids, and salicylous acid set at liberty. Dr. Ettling describes an acid salt or bisalicylite of potash having the same composition as the bibenzoate of potash; also a corresponding salt of soda, both of which form colourless acicular crystals.

Salicylimide, salhydramide $C_{42}H_{18}O_6N_2$. This body is prepared by dissolving salicylous acid in three or four times its volume of cold alcohol, and adding a quantity of aqueous solution of ammonia, equal to that of the salicylous acid employed. Yellowish white needles are immediately produced, and the liquid soon becomes a solid mass. By a gentle heat the whole is re-dissolved and crystals of salicylimide are deposited on cooling. This body is insoluble in water; it is soluble in 50 parts of boiling alcohol, but very slightly soluble in cold alcohol; its solution has a strong alkaline reaction. Solutions of alkalies and acids act upon salicylimide, with the aid of heat, as they do upon amides, reviving the ammonia and acid.

In the formation of this compound 3 atoms of salicylous acid unite with 2 atoms of ammonia, while 6 atoms of water containing all the hydrogen of the ammonia are abandoned; 2 atoms of nitrogen are thus substituted for 6 atoms of oxygen, in the formation of salicylimide. It may be represented as $3HO+C_{42}H_{15}{}^{O_3}_{N_2}$, or dividing by three:



$$HO+C_{14}H_{5}{}^{O}_{N_{\frac{2}{3}}}.$$

Salhydramidide of copper, $C_{14}H_6NO_2Cu$; or $H,C_{14}H_5NO+CuO$. This remarkable compound is represented in the last formula as a salicylous acid, in which 3 atoms of oxygen of the salicyl are replaced by 1 atom of nitrogen, and this is combined with 1 atom of oxide of copper. It is obtained in a state of purity on mixing a solution of salhydramide, the preceding compound, very dilute and slightly cooled, with the ammoniacal acetate of copper. The liquid immediately assumes an emerald green colour, and soon deposits very brilliant plates of the same colour while at the same time the liquid becomes colourless. When this salt is heated with concentrated acids, it gives a salt of copper and an ammoniacal salt, while the hydrated salicylous acid is set at liberty. Potash ley does not decompose this salt except imperfectly; sulphuretted hydrogen not more completely, even after one or two hours' action. If, however, it has first been made to boil with an acid, the decomposition by sulphuretted hydrogen is instantaneous.

Salhydramidide of iron, $3\ (H,C_{14}H_5NO)+Fe_2O_3$. This compound, which Dr. Ettling succeeded in forming, is analogous in composition to the copper compound. It precipitates in red flocks, which gradually acquire some lustre, becoming granular. Hydrochloric acid does not alter it in the cold, but when the acid is pretty concentrated and assisted with heat the compound is dissolved and salicylous acid separated.

Salhydramidide of lead. There appear to be two compounds of salhydramide with oxide of lead, but they have not been obtained in a state of purity.

Melanic acid (anhydrous), $C_{10}H_4O_5$. Salicylite of potash exposed in a humid state to air absorbs oxygen and undergoes decomposition, becoming first green and then black. The only products are acetate of potash and an insoluble black powder resembling lampblack, which Piria terms melanic acid. This acid contains no water of combination; it is soluble in alcohol and ether, and very soluble in alkalies.

Salicylic acid, $HO+C_{14}H_5O_5=HO,SaO$. This acid is produced by heating salicylous acid with an excess of dry hydrate of potash, till the brown mass becomes white, which is attended with the escape of hydrogen gas. The salicylic acid is liberated by adding an excess of hydrochloric acid, and is purified by repeated crystallizations. This acid crystallizes both from solution and sublimation very much like benzoic acid. It may be volatilised without decomposition. It is sparingly soluble in cold water, very soluble in hot water and in alcohol. It reddens vegetable colours and decomposes the alkaline carbonates. *Salicylate of silver* is an insoluble white precipitate, anhydrous. (Piria).

Chlorosalicylic acid, chloride of salicyl, chloride of spiroïle;

$C_{14}H_5O_4,Cl$. This compound is formed by passing a current of dry chlorine through dry salicylous acid. It crystallizes in yellowish oblique rhomboidal tables of a pearly lustre and peculiar aromatic odour. It fuses and sublimes unaltered. It combines directly with the alkalies, and is precipitated from these combinations by acids without undergoing the smallest change. This acid itself has been compared with the chloro-chromic, and these salts viewed as salicylates of metallic chlorides.

Chlorosalicylimide, chlorosamide, $C_{42}H_{15}Cl_3O_6N_2$; is salicylimide in which 3 atoms of hydrogen are replaced by 3 atoms of chlorine. It is a yellow mass insoluble in water, formed by directing a current of ammoniacal gas upon chlorosalicylic acid, so long as water is disengaged.

Corresponding *bromosalicylic* and *iodosalicylic* acids exist, which undergo the same transformations with ammonia.

Nitrosalicylic acid, spiroïlic acid (Lœwig); $C_{14}H_5O_8N$. Fuming nitric acid has a violent action upon salicylous acid, nitrous fumes are abundantly evolved, with the formation of a dark yellow mass, which volatilises when distilled with water; this matter has not been analysed. When, on the other hand, nitric acid of ordinary strength is digested upon salicylous acid, peroxide of nitrogen is evolved, and a crystalline mass remains, which may be purified by washing it with water and then dissolving it in alcohol. Nitrosalicylic acid crystallizes in small yellow prisms, the alcoholic solution of which dyes the skin and nails yellow; it forms crystallizable salts with the alkalies; ammonia produces with it a deep blood red colour; with the perchloride of iron it assumes a cherry red tint. Its salts have not been sufficiently examined; their probable formula is $MO+C_{14}H_4O_3, NO_4$.

CHAPTER VII.

PHLORIDZIN AND THE BODIES DERIVED FROM IT.

Formula, $C_{42}H_{29}O_{24}=C_{42}H_{23}O_{18}+6HO$, according to Mulder, Erdmann, Otto. But $C_{32}H_{15}O_{12}+6HO$, and when dried, $C_{32}H_{15}O_{12}+3HO$, according to Stass.

This substance which very much resembles salicin, was discovered by De Kœninck and Stass in the bark of the root of the apple, pear, cherry, and plum tree. It has been considered as crystallized salicin plus 2 atoms of oxygen. It is extracted from the bark cut into small pieces, by digestion in alcohol of 80 per cent, at 176°. It is crystallized by distillation of the alcohol, solution and cooling, and purified by means of animal charcoal.

Phloridzin crystallizes in colourless silky prisms of a square base, of density 1.4298, which are neutral, having a bitter astringent taste, are soluble in 1000 parts of cold water, and in all proportions in hot water, are soluble in alcohol and almost insoluble in ether. Phloridzin loses 4 atoms of water of crystallization at 212°, fuses at 320°, and is not decomposed below 392° (200° centig.). It produces a white precipitate in solution of subacetate of lead. It dissolves a large quantity of hydrate of lime, and gives by evaporation in vacuo a yellow crystalline mass, of which M. Liebig infers the composition to be $C_{42}H_{23}O_{18}+3CaO,3HO$, from an analysis by Stass. Phloridzin is a febrifuge like salicin.

Phloretin, $C_{30}H_{15}O_{10}$. When a solution of phloridzin is boiled with a little of any acid whatever, except nitric and chromic acids, it is converted into grape sugar, and the present compound, which separates from the solution as a crystalline powder. Phloridzin thus undergoes a similar change with salicin, by the action of acids.

Nitrophloretic acid, phloretic acid (Stass), $C_{30}H_{12}O_{15}N$; an uncrystallizable matter of a puce colour, obtained by the action of nitric acid on phloridzin. It is soluble in alkaline solutions, and precipitated again by acids.

Phlorizein, $C_{42}H_{29}O_{26}N_2$; a red substance soluble in ammonia, which is obtained by the joint action of air and ammonia on humid phloridzin. The addition of 8 atoms of oxygen and 2 atoms of ammonia to the elements of anhydrous phloridzin, gives exactly the composition of phlorizein. This compound also unites with 1 atom of ammonia, when dissolved in its solution and evaporated in vacuo with sticks of potash, and forms a purple blue powder, of a coppery lustre, very soluble in cold water, of which the solution has a magnificent blue colour (Stass, An. de Chim. lxix. 367).

CHAPTER VIII.

GLYCERIN.

Glyceryl, $C_6H_7=Gl$; a hypothetical radical admitted by Liebig to exist in the substance long known as glycerin, which is found combined with various acids in the fat oils. Glycerin is considered as a compound of glyceryl with 5 atoms of oxygen and 1 atom of water, or the hydrated oxide of glyceryl.

Hydrate of oxide of glyceryl, glycerin; $C_6H_7O_5+HO$. This substance was first observed by Scheele, and distinguished by him as the *sweet principle of oils*, its function in the constitution of oils and fats was developed by Chevreul, and its composition carefully determined by Pelouze*. It forms a base to the oleic, stearic, and margaric acids of the fat oils and tallow, and is separated when those acids are made to combine with an alkali or any metallic oxide, in the saponification of the oils. It is conveniently prepared in saponifying oil of olives with oxide of lead and a little water, by boiling them together; the liberated glycerin dissolves in the water, while the soap of oxide of lead is insoluble. The glycerin is accompanied by a small quantity of oxide of lead in solution, which may be precipitated by sulphuretted hydrogen. Or when an oil is converted into a soap by boiling it with water and an excess of alkali, the soap comes to the surface being insoluble in the alkaline liquor. The latter, which contains the glycerine in solution, may be drawn off, the free alkali be neutralised with sulphuric acid, and the solution evaporated to a syrup, from which strong alcohol dissolves out the glycerin. If the product is coloured it may be purified by means of animal charcoal, evaporated by a water-bath, and afterwards in vacuo over sulphuric acid.

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* Ann. de Chim. et de Phys. t. 63. p. 19.

Glycerin is thus obtained as a syrup, colourless or slightly yellow and uncrystallizable, inodorous, very distinctly sweet, of density 1.252 to 1.27, attracting moisture from the air, and miscible in all proportions with water and alcohol, but insoluble in ether. It rises in small quantity with the vapour of water, but cannot be distilled without partial decomposition. When heated in air glycerin burns with a luminous flame. It possesses an extraordinary solvent power, scarcely inferior to that of water itself. It dissolves the deliquescent salts, and many other salts which are not deliquescent, as sulphates of potash, soda and copper, nitrates of silver and potash, the alkaline chlorides, hydrates of potash and soda, and the vegetable acids. Nitric acid converts it slowly into oxalic acid; peroxide of manganese with sulphuric acid into formic and carbonic acids. Its solution in water does not undergo any change by keeping, and is not fermentable by yeast. Glycerin is decomposed when boiled with a solution of sulphate of copper, and metallic copper precipitated. It is not precipitated by subacetate of lead, but is itself when hot capable of dissolving oxide of lead. With potash it forms a compound soluble in alcohol; it combines also with barytes.

It is acted upon by chlorine and bromine; the latter forms, with hydrobromic acid, a heavy oily ethereal liquid, $C_{12}H_{11}Br_3O_{10}$, soluble in alcohol and ether. With chlorine, the product is a white solid flocculent substance, $C_{12}H_{11}Cl_3O_{10}$.

Acid sulphate of oxide of glyceryl, sulphoglyceric acid; $HO.\,C_6H_7O_5+S_2O_6$. When glycerin is mixed with twice its weight of concentrated sulphuric acid, combination takes place with the evolution of much heat, but without charring. The liquid when diluted and neutralised with carbonate of lime gives a precipitate of sulphate of lime, which is separated by filtration, while sulphoglycerate of lime remains in solution. The acid may be isolated by cautiously precipitating the lime by means of oxalic acid. But it cannot be preserved, for it is gradually decomposed and converted into hydrate of oxide of glyceryl and sulphuric acid; the change takes place still more rapidly when the liquor is slightly heated. Even when newly prepared, this acid liquid precipitates lime and barytes from their salts.

Sulphate of oxide of glyceryl and lime, $CaO.C_6H_7O_5+S_2O_6$, (Pelouze.) It is deposited from its solution evaporated to the consistence of a syrup in prismatic needles or colourless plates, which are insoluble in alcohol and ether. The salt of *lead* has a composition analogous to that of lime. The solutions of both of these salts are decomposed by ebullition, and resolved into insoluble sulphates and hydrated oxide of glyceryl.

M. Liebig makes the remark that oxide of glyceryl probably exists in nature combined with other acids besides those of the fats. Thus a *benzoate of oxide of glyceryl* would possess the same composition as picrotoxin; mannite even might be an oxide of glyceryl. (Traité, I. 602.)

CHAPTER VIII.

ETHAL, AND THE CETYL SERIES OF COMPOUNDS.

Spermaceti differs from the other natural fats in affording a peculiar substance, first observed by Chevreul, instead of glycerin, when saponified by an alkali. This substance was named ethal* by MM. Dumas and Peligot, who consider it the alcohol of a new series of compounds, of which the radical is cetyl; or ethal is the hydrate of oxide of cetyl.

Formula of *cetyl* $C_{32}H_{33}$=Ct. Has not been isolated.

Hydrate of oxide of cetyl, ethal; $C_{32}H_{33}O+HO$. To liberate ethal from spermaceti, the latter is digested with an equal weight of hydrate of potash dissolved in 2 parts of water, at a temperature not exceeding 200° for several days. The soap thus formed which consists of oleate and margarate of potash with ethal, is then decomposed by dilute sulphuric acid, which gives a fatty mass, composed of the oily acids and ethal in a state of mixture and not of combination; it is washed well with boiling water, and then boiled with barytes water in excess, which forms insoluble soaps with the oleic and margaric acids; and ethal is dissolved out by means of cold alcohol, which is afterwards distilled off. The ethal is dissolved in ether, to separate a trace of adhering barytic salts.

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* A word formed of the first syllables of *ether* and *alcohol*.

Ethal is deposited from an alcoholic solution in crystalline plates; it fuses above 118°, and solidifies at that temperature, forming a white crystalline mass. It is volatile, and may be distilled without decomposition. It is insoluble in water, soluble in alcohol and ether, neutral and does not combine with acids or alkalies. It is decomposed by nitric acid, and combines with sulphuric acid.

Chloride of cetyl; $C_{32}H_{33},Cl=CtCl$.—An oily liquid, formed by the action of perchloride of phosphorus on ethal.

Acid sulphate of oxide of cetyl; $HO.CtO,S_2O_6$.—This compound is formed when ethal is heated with strong sulphuric acid. It forms double salts when neutralised with bases. *Sulphate of oxide of cetyl and potash*, $KO.CtO,S_2O_6$, is prepared by adding an alcoholic solution of hydrate of potash to the preceding compound, sulphate of potash precipitates, and the salt in question remains dissolved in the alcohol, from which it is deposited in white pearly scales. (Dumas and Peligot, Annales de Chimie, &c., lxii, 5.)

Ethalic acid, $HO+C_{32}H_{31}O_3$. This compound, the acetic acid of the cetyl series, was formed by M. Dumas, by mixing 1 part of ethal with 5 or 6 parts of the mixture of hydrate of potash and quicklime, and heating to 410° or 428° (210° or 220° centig.), for five or six hours. Hydrogen gas is evolved, and the ethalate of potash formed. The last is decomposed by hydrochloric acid, and the ethalic acid, which separates in flocks, purified by boiling it with the acid liquid, and repeatedly with water, converting it into ethalate of barytes, and treating the last with boiling alcohol, to dissolve out undecomposed ethal. The ethalate of barytes is then decomposed by hydrochloric acid, and the liberated ethalic acid purified by solution in ether.

Ethalic acid is solid, white, inodorous, tasteless, lighter than water. Fused by heat, it solidifies at 101°, and then presents itself in the form of small brilliant needles, in groups radiating from a centre. It is insoluble in water, but is dissolved largely by alcohol and ether. When heated in a little capsule, it boils like ethal, and is volatilised without leaving any residue.

All the *ethalates* are insoluble in water or alcohol, except those of potash, soda, and ammonia. The insoluble ethalates are prepared by precipitating the metallic salts dissolved in alcohol, by an alcoholic solution of ethalate of potash or soda. The ethalates of the alkalies are decomposed by a large quantity of water, although they dissolve in a small quantity without change. (Dumas and Stas, An. de Chim. &c. lxxiii, 124).

Cetene, $C_{32}H_{32}$. This hydrocarbon was obtained by MM. Dumas and Peligot, by distilling ethal repeatedly with glacial phosphoric acid, which deprives the former of 2 atoms of water. It is an oily, colourless liquid, boiling at 527°; the density of its vapour is, by experiment, 8007; by calculation, supposing its combining measure 4 volumes, 7843. It is insoluble in water, soluble in alcohol and ether.

CHAPTER VII.

OTHER INDIFFERENT SUBSTANCES.

CLASS I. ORDINARY CONSTITUENTS OF PLANTS.

SECTION I.

PECTIN.

Formula: $HO + C_{12}H_{17}O_{11}$. This name was applied by Braconnot to a principle which forms the basis of vegetable jelly.* It is extensively diffused in the juices of pulpy fruits and roots, especially at the time of their maturity, and occasions these juices to coagulate, when mixed with alcohol or boiled with sugar. It may be prepared from apples, for instance, by heating the juice with a little albumen till the latter coagulates, filtering, and precipitating the pectin by a considerable addition of alcohol to the liquid. By a second solution in water, and precipitation by alcohol, the pectin is completely purified. When only a small quantity of alcohol is added to the watery solution, the juice fixes as a jelly after an interval of one or two days.

After being washed on a filter and dried, pectin is semitransparent, and has a considerable resemblance to isinglass. It is insoluble in alcohol, soluble in water, the solution is neutral to test paper, insipid or tasteless; it is not adhesive like gum arabic. The dried pectin swells up in water, and more readily in cold than in hot water; with one hundred times its weight of water it forms a jelly, with a larger quantity only a gelatinous liquid. It resembles vegetable mucilage in many of its properties; with nitric acid it first forms saccharic acid, afterwards mucic acid. It is dissolved by an excess of alkali, and converted into the following isomeric acid.

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* From *πηκτις, coagulum.*

Pectic acid. This substance is conveniently obtained by grating yellow carrots to a pulp, expressing the juice, washing the marc several times successively with distilled or rain-water, and expressing it well again. The marc is then diffused through six times its weight of pure water, free from earthy salts, and solution of pure caustic potash gradually added by small portions. The mixture is then heated and made to boil for about a quarter of an hour, and the boiling liquor filtered through a cloth. The mixture is known to have boiled long enough, when a small portion of it, after being filtered, is found to become a jelly on adding to it a drop or two of acid.

The pectic acid may be separated by a strong acid, but as it is then difficult to wash, it is preferable to precipitate it by chloride of calcium, which gives the pectate of lime, in the form of a coagulated jelly completely insoluble in water. This jelly is washed on a cloth, boiled with water, to which a little hydrochloric acid is added, which dissolves the lime and leaves the pectic acid; the last is then washed with cold water. Pectic acid remains as a transparent and colourless jelly, faintly acid, very slightly soluble in cold water, but more soluble in boiling water. The filtered solution does not become solid on cooling, but it coagulates and forms a jelly when alcohol is added to it, or sugar, which has the property of dissolving pectic acid, and transforming it after some time into a jelly, a property on which is founded the preparation of the jelly of currants, apples, gooseberries, &c.; fruits of which the juice mixed with sugar coagulates in the course of a few days. When evaporated to dryness, pectic acid resembles pectin in appearance, and has the same composition. It is a bibasic acid. The *pectates* possess the property of forming a jelly when precipitated, in common with the acid. Those only containing an alkaline base are soluble in water, and they dissolve only in the latter when pure and free from acid or earthy salts. (Berzelius, Traité II. 367 and 467.)

By boiling it with an excess of caustic alkali, pectic acid is again modified, and converted into another acid, which dissolves easily, is very fluid and has a sour taste. This second acid is also isomeric in its salts with pectin.

SECTION II.

VOLATILE OR ESSENTIAL OILS AND RESINS.

These oils or essences occur in all smelling plants, and are the source of the fragrance of the vegetable kingdom. Some plants, such as thyme, contain a volatile oil in all their parts; in others the oil is confined to particular parts, such as the flower, the pollen, the leaves, the root or the bark. In most plants the oil is contained in little sacs or vesicles, so well closed that the plant may be dried without evaporation of the oil, and the latter is preserved for years from the influence of the air. In other species, and particularly in flowers, the oil is constantly produced at the surface, and dissipated by evaporation the moment of its formation. Essential oils are generally obtained by distilling the plant with water. They are themselves less volatile than water, but are carried over with the steam, owing to the sensible tension of their vapour at 212°, and condensing in the refrigeratory are found on the surface of the distilled water or at the bottom of the vessel. A few oils are obtained by expression, such as those of the oranges and lemons, where the oil resides in the epidermis of the fruit. Some other oils which are not contained in vessels, such as those of violet, jasmine, &c. are obtained by maceration of the flowers in an inodorous fixed oil, and are used in this state in perfumery, or are afterwards obtained apart by distilling the fixed oil with water.

The essences are generally liquid, but occasionally solid at the usual temperature; they have all a strong odour, more or less agreeable, which is somewhat harsh immediately after distillation but improves with keeping, although in general the odour is never so agreeable as that of the fresh plant. Their taste is acrid and burning, or only aromatic when it is greatly weakened by mixing them with other substances. Some of these essences are colourless, most of them yellow, red or brown, others green, and a small number are blue. They are not unctuous to the touch like the fixed oils, but feel harsh. They produce an oily stain upon paper which disappears on drying. Their density varies from 0.759, the density of oil of coriander, to 1.096, the density of oil of sassafras; but they are generally lighter than water. Although volatile at the ordinary temperature, their boiling point is usually not under 320°. The volatile oils are nearly all decomposed in part when distilled alone. They burn in air with a bright but smoky flame. When exposed to cold they freeze, but generally separate into a solid and fluid portion, indicating that they are mixtures of two oils differing in fluidity; the concrete portion is termed the *stearopten*, and the liquid portion the *elaopten* of the oil.[*]

The essences exposed to air deepen in colour and absorb oxygen. It has been observed that the odour of oils is closely related with this chemical change. Those which oxidate most rapidly have the strongest smell, and the characteristic odour of no oil can be perceived immediately after its distillation in an atmosphere of carbonic acid gas. The oil becomes in time thick, loses its odour, and is transformed into a resin which in the end becomes hard. A small quantity of carbonic acid is formed in this transformation, but no water; it is greatly promoted by light. An oil which has commenced to undergo this change consists of a portion of oil unchanged, holding a resin in solution, from which the former may be separated by distillation with water. The substance turpentine is in this condition, and gives oil of turpentine, when distilled, with common resin as the fixed residue. Essences should therefore be preserved in well-stopt bottles. They are strongly acted upon and frequently inflamed by concentrated nitric acid. Some of them produce a sort of explosion when mixed with dry iodine.

Essential oils are very slightly soluble in water, but sufficiently so to communicate their odour and taste to that liquid. Water which has been distilled from an odoriferous plant is a saturated solution of the oil; the *distilled waters* used in medicine are so prepared. These liquors are improved by a second distillation, or by keeping for some time in a cool place when contained in opaque vessels imperfectly closed, during which some foreign matters which have been distilled along with the oil, disappear. The volatile oils are all very soluble in alcohol, and the more so the less water it contains. With alcohol of 0.820, oil of turpentine may be mixed in a large proportion, and such a liquid is sometimes burned in a lamp properly constructed for the purpose. The oils which contain oxygen, such as those of lavender and peppermint, dissolve more readily in aqueous alcohol than the pure hydrocarbons. Such solutions of essential oils in alcohol are *lavender water*, *eau de Cologne*, &c. They are rendered turbid by water, which combines with the alcohol and liberates the oil. Essential oils are soluble in ether. They are capable of dissolving at a high temperature a considerable quantity of sulphur and a small portion of phosphorus; and may be combined or mixed with bisulphuret of carbon, chlorides of sulphur, of phosphorus, of carbon and arsenic. They combine with several vegetable acids, such as acetic, oxalic, succinic acids, the oily acids, camphoric and suberic acids. With the exception of oils of cloves, cinnamon and cedar wood, the volatile oils do not combine with salifiable bases; they differ entirely in this respect from the fixed oils which are saponified by alkalies. After being brayed with sugar the volatile oils dissolve better in water. Volatile oils dissolve all the fat oils, resins, and animal fats.

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[*] These terms were first applied to the solid and fluid portions of fixed oils; they are derived from *στεαρ* suet and *ελαιον* oil.

Many volatile oils contain no oxygen, and in all of these, with one or two exceptions, the carbon and hydrogen are C_5H_4, or some multiple of these numbers; but the larger proportion are oxides. Several of the latter part with their whole oxygen, with a proportional quantity of hydrogen, as water, under the action of anhydrous phosphoric acid, and are converted into pure oily hydrocarbons.

A. ESSENTIAL OILS CONTAINING NO OXYGEN.

OIL OF TURPENTINE.

Formula: $C_{20}H_{16}$. It is derived from several kinds of turpentine, a semi-fluid resin exuding from the different species of the pine. The turpentine is distilled with water, the oil comes over, and a resin remains behind. The oil met with in commerce generally contains some resin, produced by the oxidation of the oil, from which it should be purified by rectification, that is, a second distillation from water. The pure oil is a colourless, thin liquid, having a peculiar odour, of which the density is 0.872 at 50°, and boiling point 314°.2 (156°.8 centig.) The specific heat of this liquid is 0.462, according to Despretz, that of water being 1.000. The density of its vapour is 5010 by experiment, 4763 by calculation. It abandons only half the heat when condensed from the state of vapour at its boiling point, that vapour of water does at 212°; but a portion of that heat is heat of temperature, for the latent heat of vapour of oil of turpentine is to that of vapour of water only as 0.313 to 1.000. When cooled to —16°.6, oil of turpentine deposits its stearopten in white crystals, which are heavier than water, and fuse at 19°.4 (—7° centig.)

Oil of turpentine is certainly a mixture of two or more isomeric oils; this appears in its forming two compounds with hydrochloric acid, one of which has long been known as *artificial camphor*. To prepare this compound, well dried hydrochloric acid gas is made to pass slowly into the essence surrounded by ice. Without this precaution, it becomes hot, and the hydrochloric acid is not so completely absorbed. It is left to itself for twenty-four hours, after which, a quantity of a white crystalline substance is found deposited in a brown fuming mother-liquor. The composition of the solid hydrochlorate is represented by $C_{20}H_{16}+HCl$. The name *camphene* being applied to the essence by Dumas,* this is the *hydrochlorate of camphene*. When pure, it is a snow-white substance, of a peculiar odour, suggesting that of common camphor, but very different in other respects; fusible above 212°, and volatile; alcohol of 0.806 dissolves at 57° one third of its weight of it. It is decomposed completely when distilled rapidly by means of an oil-bath, with two or three times its weight of quicklime, chloride of calcium being formed, and a colourless oil, of the same composition and density as oil of turpentine, which can be united again with hydrochloric acid, and gives an entirely solid product. This oil, however, is not identical with the essence, differing from it in its optical properties, and is distinguished as *camphilene* (Deville). The liquid hydrochlorate is of density 1.017, and its composition is also expressed by $C_{20}H_{16}+HCl$. (Soubeiran, Capitaine).

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* The essence of turpentine may be allowed, as the base of artificial camphor, to retain this name.

It is difficult to decompose the hydrochlorate of turpentine completely by an alkali; a portion of it distils over and contaminates the oil thus obtained. M. Deville adds gradually to essence of turpentine kept cold, a small quantity, about $\frac{1}{10}$th of oil of vitriol, so that the whole becomes deep red and viscid after strong agitation, allows it to deposit for twenty-four hours, and decants the thick liquid from a black deposit. This red liquid, when heated, emits some bubbles of sulphurous acid, becomes colourless, and is transformed into a mixture of two oils, which he names terebene (from terebenthine), and colophene. The former distils over first. *Terebene* has the same composition and density as camphene, but differs from the latter in its rotatory power on polarised light being equal to nothing. By treating terebene by hydrochloric acid, Deville obtained a new liquid, *sub-hydrochlorate of terebene*, of density 0.902 at 59°, with a good deal of the odour of terebene itself; its composition $2C_{20}H_{16}+HCl$. A corresponding *hydrobromate* of terebene was a colourless liquid, of density 1.021 at 75°.2 (24° centig.); its composition $2C_{20}H_{16}+HBr$. The solid *hydrobromate of camphene*, formed by the action of hydrobromic acid on the essence is $C_{20}H_{16}+HBr$. It preserves, in common with the solid hydrochlorate, the negative rotatory power of the essence. The liquid hydrochlorate, prepared from the essence, loses that property, and is, therefore, supposed not to contain camphene but terebene, and named *hydrochlorate of terebene*. When hydrochlorate of terebene is distilled with an alkali, it gives an isomeric oil, *terebilene*, having the same relation to terebene that camphilene has to camphene. Two corresponding hydriodates of terebene have been formed.

A very regularly crystallized substance has often been found in old oil of turpentine, or in oil of turpentine left long in contact with dilute nitric acid, which appears to be formed by the assimilation of the elements of water. Its composition is $C_{20}H_{22}O_6$, or represented as a *hydrate* of oil of turpentine $C_{20}H_{16}+6HO$. (Dumas and Peligot). It is fusible about 302° (150° centig.), and sublimes. Soluble in 200 parts of cold, and in 22 parts of boiling water, from which it crystallizes on cooling.

By treating terebene by chlorine, M. Deville formed two liquid chlorinated compounds, which he names *chloroterebene*, $C_{20}H_{12}Cl_4$; and *monochloroterebene*, $C_{20}H_{14}Cl_2$. He also formed *bromoterebene*, $C_{20}H_{12}Br_4$. Terebene does not form a hydrate like the essence. The essence treated with chlorine gives a chlorinated compound, which M. Deville names *chlorocamphene*, of the same composition as chloroterebene, but differing in density and other properties.

Colophene is an additional product besides terebene, of the action of concentrated sulphuric acid upon the essence. It distils over after the terebene, on urging the heat so as to bring the viscid mass in the retort to a state of strong ebullition, as a viscid oil, of a clear yellow colour, which re-distilled several times alone, and once (if contaminated with sulphur) from the alloy of potassium and antimony, constitutes colophene. Colophene is colourless by transmitted light, but possesses a kind of dichroism and may be seen of a deep indigo blue colour, a property which can be recognised in all its compounds. Its density is 0.940 at 48°, and 0.9394 at 77°. It is isomeric with the essence of turpentine. Its boiling point is about 590 or 600°; the density of its vapour could not easily be taken with exactness, but was certainly not less than twice that of oil of turpentine. Assuming the density as double, the atom of colophene will be $C_{40}H_{32}$, its combining measure 4 volumes. This oil is also one of the products of the rapid distillation of colophony or the resin of turpentine, and was named colophene on that account.

Colophene absorbs hydrochloric acid, but the *hydrochlorate* is a feeble combination, and is deprived of its acid by chalk. By distilling the impure hydrochlorate from barytes, M. Deville obtained an isomeric oil, which he considers the *colophilene* of colophene. It did not appear, however, to possess the dichroism of the latter body. Colophene also absorbs chlorine with avidity, without any disengagement of hydrochloric acid, and is converted into a resin, soluble in alcohol and crystallizable, having very much the appearance of colophony, and which is named *chlorocolophene*, $C_{40}H_{32}Cl_4$. It is in fact colophony in which 4 atoms of oxygen are replaced by 4 atoms of chlorine. Fused by heat, and exposed again to chlorine chlorocolophene absorbs that gas, and emits a large quantity of hydrochloric acid, giving a new product, of a transparent yellow colour, which may be represented by $C_{40}H_{24}Cl_8$.

It thus appears that four isomeric oils exist related to the essence of turpentine, of which the common formula is $C_{20}H_{16}$, namely camphene, terebene with camphilene and terebilene, the two latter being obtained by similar processes from the two former; also another pair, of which the atomic weight is double and the formula $C_{40}H_{32}$, namely colophene and colophilene; and that each of these bodies gives rise to a particular series of compounds by uniting with hydrochloric acid, chlorine, &c. (Deville, An. de Chim. lxxv, 37).

COLOPHONY, OR RESIN OF TURPENTINE.

Common turpentine affords when distilled with water from 5 to 25 per cent of essence, what remains being common resin, named colophony, or colophonium, of which the composition generally received is $C_{40}H_{32}O_4$ (Rose); that is, 2 equivalents of the essence combined with 4 equivalents of oxygen. M. Liebig is disposed, from more recent analyses, to represent the resin by $C_{40}H_{30}O_4$, and then in its formation, the essence $C_{40}H_{32}$ loses 2 atoms of hydrogen, which are replaced by 4 atoms of oxygen. The resin is not, however, a homogeneous product, but was divided by M. Unverdorben into two different resins, which he named *sylvic* and *pinic acids*. The properties of the mixture of these resins or colophony are familiar; it is a yellowish brown, translucent, brittle solid, fusible, readily soluble in alcohol, ether, the fixed and volatile oils; soluble in alkaline leys, with which it combines as an acid, and forms soluble salts, which are detergent, and enter largely into the composition of all brown soaps. The two resins are separated from each other by means of cold alcohol, of 72 per cent (sp. gr. 0.867), which dissolves pinic acid, or alpha-resin as it is also called, and leaves behind sylvic acid, or beta-resin.

Alpha-resin (pinic acid), is precipitated from the alcoholic solution by water; it is not crystallizable; after being fused, it has quite the appearance of colophony; it is insoluble in water, but dissolves easily in alcohol, ether, and oil of turpentine;

these solutions have an acid re-action. The pinates of potash, soda and ammonia dissolve in water, but are precipitated by an excess of alkali or the addition of any alkaline salt. The pinates of other bases are insoluble in water, and may be precipitated from alcoholic solutions of the alkaline pinates by double decomposition, employing an alcoholic solution of the other salt; they are most frequently insoluble in alcohol, but many dissolve in ether. The composition of pinic acid was found by Rose to be $C_{40}H_{32}O_4$, or the same as that of colophony ($C_{40}H_{30}O_4$, according to Liebig). Sylvic acid has likewise the same composition.

By distilling or heating pinic acid, a new resin is formed, *colopholic acid*, of the same composition, but possessing a stronger affinity for bases.

Beta-resin (sylvic acid). The insoluble residue treated with boiling alcohol, dissolves entirely; it is filtered hot, and crystallizes on cooling. It is purified by a second crystallization, particularly from alcohol containing a little sulphuric acid. It is transparent and colourless, crystallizes in rhomboidal prisms, terminated by four facets, which are generally very thin, and so large as to resemble tables. It fuses below 212°, is insoluble in water, but dissolves easily in alcohol, ether, the fixed and volatile oils. Alcohol of 72 per cent takes up, when boiling, one third of its weight, but abandons nearly the whole on cooling in a crystalline form. It is dissolved by concentrated sulphuric acid, and precipitated again by water from that solution, but in the condition, according to Unverdorben, of pinic acid. The *sylvates* of *potash*, *soda* and *ammonia* are soluble in water; the sylvates of other bases are insoluble in water, but frequently dissolve in ether and even alcohol. The sylvate of *magnesia*, in particular, is soluble in alcohol. The addition of ammonia, even in excess, to the solution of sylvic acid in alcohol does not throw down a precipitate, and the acid precipitated by water dissolves readily in ammonia; so also does the resin in caustic potash, but an excess of the latter throws down a *subsylvate of potash*, a compound very slightly soluble in an excess of base. The composition of sylvic acid is $C_{40}H_{30}O_4$, or half these numbers, according to Tromsdorff.

These two resins form the large proportion of colophony, but a third resin has been observed in it, which is indifferent, soluble in cold alcohol, but not precipitated by the acetate of copper.

The white resin, *galipot*, derived from the pinus maritima, consists almost entirely of a colourless, crystallizable resin, named ***pimaric acid***, $C_{40}H_{30}O_4$, of the same composition as the preceding resins, but differing from them in properties. When the crystallized resin is dissolved in alcohol, it soon separates as an amorphous powder, which is much less soluble, without alteration in composition. When distilled in vacuo, pimaric acid is converted into another resin, ***pyromaric acid***. Boiled for a long time with nitric acid, pimaric acid gives rise to a new acid, containing nitrogen, ***azomaric acid***, $C_{40}H_{18}O_{12}N+4HO$, of which the capacity of saturation is double that of pimaric acid. (Laurent, An. de Chim. lxxii, 383).

By the dry distillation of colophony, M. Fremy obtained a heavy light-coloured oil, almost destitute of taste and smell, boiling above 482°, which he named ***resinein***. Its composition is expressed by $C_{20}H_{15}O$; and it appears to be formed by the abstraction of an atom of water from half an equivalent of colophony. By distilling purified resin with eight times its weight of slaked lime, the same chemist procured two liquid products, ***resinone*** $C_{10}H_9O$, soluble in alcohol, and boiling at 172°.5; and ***resineone*** $C_{23}H_{18}O$, less soluble in alcohol, and boiling at 298°.5 (Liebig, Annalen, xv, 282).

By distilling resin at a higher temperature. MM. Pelletier and Walter obtained a liquid, ***retinaphtha*** C_7H_4; which gives with chlorine a compound $C_{14}H_6Cl_2$. At the same time with retinaphtha, a less volatile liquid, ***retinyle***, C_9H_6, is formed. The less volatile product of the distillation of resin affords a liquid ***retinole***, C_8H_4, with a solid compound ***retisterene*** or metanaphthaline, which is isomeric with naphthaline. (Ann. de Chim. &c. lxvii, 269).

Common resin is converted into shoemaker's resin, or Burgundy pitch, by heating it repeatedly with water, and going to dryness.

Oil of lemons, $C_{10}H_8$. This essence is extracted from the rind of the lemon (*Citrus medica*), usually by expression. The crude oil is pale yellow, but when rectified it is colourless, has a strong smell of lemons, density 0.847, and boiling point

343°.4 (173° centig.). It has absolutely the same composition in 100 parts as essence of turpentine, but only half the atomic weight. It forms, with hydrochloric acid both a solid and liquid compound, according to Blanchet and Sell. The composition of both is expressed by $C_{10}H_8,HCl$. The camphor and also the liquid hydrochlorate of lemon oil are decomposed by means of alkalies, and furnish two oils, which possess the same composition as the essence employed. *Oil of oranges*, from orange-peel (*Citrus aurantium*) differs only in smell from oil of lemons. *Oil of neroli*, or of orange-flower is quite different, and is in great part soluble in water. It appears to contain a stearopten, but its composition is not exactly known.

Oil of junipers.—Obtained by the distillation of crushed juniper-berries with water. It is colourless, and possesses the taste and odour of juniper; is composed of two oils of different volatility, both of them containing carbon and hydrogen in the same relation as all the oils of this class, namely C_5H_4. By adding a little of this oil to brandy, gin or Hollands are formed.

Savin-oil.—Derived from the berries of *Juniperus sabina*, colourless, also represented by some multiple of C_5H_4. Both of these oils are used as diuretics.

Oil of copaiba, $C_{10}H_8$. The balsam of copahu or copaiva is extracted in Brazils and the Antilles from several plants, of the genus *copaïfera*. It is obtained by incision, in the same way as common turpentine, with which it has a great analogy; and is a clear-yellow, transparent, thick liquid, consisting of a resin and volatile oil.

The oil is colourless, thin, of an aromatic but disagreeable odour, of density 0.878, and boiling point 473°. Absolute alcohol dissolves two-fifths of its weight of this oil, but twenty-five parts of the spirits of wine of commerce, are required to dissolve one part. It forms a crystallizable compound with hydrochloric acid; it is isomeric with oil of lemons, and has the same mode of condensation. (Blanchet).

Copahuvic acid, $C_{40}H_{32}O_4$. This name is applied to the resin of copaiva, which possesses, according to Rose, the same composition as colophony. To obtain it crystallized, M. Schweizer dissolves 9 parts of the balsam in 2 parts of ammonia, and leaves the mixture in a cool place. The crystals which form being taken out, washed with ether, and re-dissolved in alcohol, furnish the pure resin by spontaneous evaporation; the salt of copahuvic acid and ammonia loses its ammonia during the evaporation. The *copahuvates* of *potash* and *soda* are soluble in water, that of *ammonia* soluble in ether and alcohol, but not in water. The salt of *silver* is crystallizable.

Oil of pepper, from *Piper nigrum*, has the same composition as oil of copaiva, and is similar in properties.

Oil of cubebs, from *Piper cubeba*, is supposed by Soubeiran and Capitaine to be $C_{15}H_{12}$, its compound with hydrochloric acid being $C_{15}H_{13}Cl$. The former is still a multiple of C_5H_4.

Oil of storax, from the balsam storax liquida, by distillation, has, according to Marchand, its carbon and hydrogen as C_2H, or in the same relation as benzole, and therefore differs in composition from all other known essential oils. It is converted by nitric acid into a resinous body, which yields a particular crystallizable oil, by distillation, the *nitrostyrole* of Simon.

Oil of elemi, obtained by distilling the resin, is a transparent colourless liquid, of an agreeable smell, its density is 0.852 at 75°.2 (24° centig.); it absorbs hydrochloric acid, but does not seem to form a solid camphor. It consists of carbon and hydrogen in the proportion of C_4H_5. (Stenhouse.)

Laurel-turpentine oil, imported of late from Demerara under the name of laurel oil; its density is 0.8645 at 60°, it begins to boil at 301°, but its boiling point rises to 325°. Its smell slightly resembles that of oil of turpentine, but is much more agreeable and approaches that of oil of lemons. It contains no oxygen, and consists of two or more isomeric oils of the C_5H_4 type. This oil is an excellent solvent of caoutchouc, and is employed as an external application in rheumatism. (Stenhouse.)

B. ESSENTIAL OILS CONTAINING OXYGEN.

Oil of bergamotte is obtained from the ripe fruit of the *Citrus bergamotta*, or *Citrus limetta* (the lime). It is yellowish, but when rectified, colourless, has an agreeable odour, and is much used as a perfume. Its density is 0.862; it combines with hydrochloric acid. It was found by Ohme to contain 7.098

per cent of oxygen, and considered as a hydrate of lemon oil, $3C_{10}H_8+2HO$. But MM. Soubeiran and Capitaine find it to be a mixture of 2 or more oils, which differ in volatility, but could not be completely separated, with the proportion of oxygen varying from 3.37 to 16.14 per cent. By the action of anhydrous phosphoric acid upon this essence, an oil is obtained which has the same composition as oil of lemons, or is of the C_5H_4 type. By the action of phosphoric acid on the impure oil a peculiar acid was also produced (named *phospho-bergamic acid),* which forms soluble salts with lime and oxide of lead.

Oil of cloves, from the undeveloped flower-buds of the *Caryophyllus aromaticus*. It is colourless or yellowish, becoming brown in air, of a strong odour and burning taste; its density is 1.061. Clove oil consists of two different oils, one light, of the C_5H_4 type, the other heavy, of density 1.079, and boiling point 469°. 4 (243°. centig.) which forms crystalline compounds with bases, and is named *caryophyllic acid*. The two oils are separated by distillation of the crude oil with a solution of potash, by which the heavy or proper clove oil is retained in combination, and may afterwards be liberated by means of sulphuric acid. Alcohol also extracts from cloves a solid substance, *caryophylline*, of which the formula, according to both Dumas and Ettling, is $C_{20}H_{16}O_2$. The distilled water of cloves deposits another substance in yellowish pearly scales, which has been named *eugenine* by Bonastre.

Oil of anise, from *Pimpinella anisum*, is yellowish or colourless, of density 0.9857. It contains so much stearopten that it is solid at the usual temperature.

The stearopten obtained by pressure of the oil cooled to 32°, crystallizes in colourless plates, fuses about 64°, and boils at 431°.6. Its composition, according to the latest determination of M. Cahours, is $C_{20}H_{12}O_2$. With chlorine it appears to form two semifluid compounds of a viscid consistence, $C_{20}H_9Cl_3O_2$, and $C_{20}H_{7\frac{1}{2}}Cl_{4\frac{1}{2}}O_2$. With bromine the action is more definite, and a crystalline compound is formed, *bromanisal*, $C_{20}H_9Br_3O_2$. If 1½ parts of sulphuric acid are digested with 1 part of the concrete essence, the latter is entirely converted into a substance of a resinous nature, which when purified from sulphuric acid by distillation, is termed *anisoïne*, by Cahours. It is a perfectly white inodorous substance, fusible at a temperature above 212°, of which the formula is $C_{20}H_{12}O_2$, or it is isomeric with the original concrete essence. By the action of dilute nitric acid on the essence of anise, *anisic acid*, $HO+C_{16}H_6O_5$, is formed, which crystallizes in fine needles and is volatile without decomposition; it belongs to the class of benzoic and cinnamic acids. When distilled with an excess of barytes, hydrated anisic acid loses 2 atoms of carbonic acid and yields *anisole* $C_{14}H_7O_2$, a colourless highly mobile liquid, boiling above 302° (150° centig.), of an agreeable aromatic odour, insoluble in water, soluble in alcohol. Anisole gives crystallizable and volatile compounds with chlorine and bromine; it is evidently allied to benzole. Boiled with stronger nitric acid the concrete essence of anise, gives *nitranisic acid*, $HO+C_{16}H_5NO_9$. *Nitraniside* is a yellow resinous substance, produced by the action of fuming nitric acid upon the concrete essence; its probable formula is $C_{20}H_{10}N_2O_{10}$. (Cahours, Ann. de Chim., &c., 3 sér. ii, 274.)

The concrete essences of *fennel* and *badian* are found by Cahours to be absolutely identical with that of anise. The concrete essence of anise is not affected by alkalies, in which respect it differs from camphor, the solid essence of cedar, oil of mint and certain other essences.

Oil of bitter fennel consists principally of two oils, one possessing the composition of the concrete essence of anise; and the other and more volatile oil which is much more difficult to purify, appearing to correspond in composition with essence of lemons and turpentine, but perhaps with a different state of condensation. The more volatile portion, when exposed to a slow stream of *deutoxide of nitrogen*, becomes thick and turbid, and alcohol then throws down from it a white silky matter, of which the composition is $C_{15}H_{12}N_2O_4$. (Cahours.)

Oil of hyssop from the *Hyssopus officinalis*, begins to boil at 288°, but its boiling point rises to 325°. It is a mixture of several oils, one of which probably contains no oxygen, as by repeated rectification of a portion of the oil containing 9 per cent of oxygen with fused potash, the quantity of oxygen was reduced to 1¾ per cent, the greater part of the oxygenated oil being converted into a brownish resin. (Stenhouse.)

Cajeput oil, $C_{10}H_9O$, is obtained from the leaves of the *Mela-*

leuca leucadendron of the Moluccas. In the crude state it is green, but becomes colourless by rectification.

Oil of caraways, extracted from the seeds of the *Carum carui*, contains two different oils, one of which is probably a hydrocarbon (Voelkel). These are different from the oils of the *Cuminum cymimum*, although the two plants belong to the same family.

Oil of cummin is extracted from the seeds of the *Cuminum cymimum*. The Roman oil was found by M.M. Gerhardt and Cahours* to consist of two oils. One of these oils they have distinguished as *cymene;* it is a hydrocarbon $C_{20}H_{14}$, and boils at 329°. The other contains oxygen, and appears to be the hydruret of a compound radical like benzoyl, which may be named *cumyl.* Cymene is separated by dropping the essence into hydrate of potash in a state of fusion, the hydrocarbon distils over, and the hydruret of cumyl is retained by the alkali as cuminic acid. The known compounds of cumyl are as follows:

Hydruret of cumyl, or cuminol .	$C_{20}H_{11}O_2+H$
Cuminic acid	$C_{20}H_{11}O_2+O$
Chloride of cumyl or chloro-cuminol	$C_{20}H_{11}O_2+Cl$
Bromide of cumyl or bromo-cuminol	$C_{20}H_{11}O_2+Br$
Hydrated cuminic acid . .	$C_{20}H_{11}O_2+O+HO$.

Hydruret of cumyl or *cuminol* is a colourless or yellowish liquid of a strong odour, easily altered by the contact of oxygen when heated. Its boiling point is 428°; density of its vapour by experiment 5240, by calculation 5094, its combining measure being supposed four volumes. Cuminol is capable of uniting with hydrate of potash at the ordinary temperature without the evolution of hydrogen. It is oxidated and converted into *cuminic acid* by direct oxidation, or when treated with caustic alkali in which case hydrogen is evolved, or by the action of sulphuric acid and chromate of potash. This acid, which corresponds with benzoic acid, is colourless, crystallizes in prismatic needles, has an acid burning taste, is scarcely soluble in water, dissolves easily in alcohol, and may be sublimed. When hydrated cuminic acid is distilled with 4 parts of caustic barytes, it yields an aromatic colourless liquid, $C_{18}H_{12}$, to which the name *cumene* has been applied; it boils at 291°.2 (144° centig.) Cumene is analogous to benzin or benzole; it forms with fuming sulphuric acid *sulphocumenic acid*, corresponding with sulphobenzic acid, of which the barytic salt is crystallizable. With nitric acid it forms *nitrocumide*, analogous to nitrobenzide.

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* Recherches chimiques sur les huiles essentielles. An. de Chim. 3me Série, t. i. p. 60.

Cymene has been found to correspond perfectly in density, boiling point, and density of vapour with *camphogen* from camphor, and is believed to be identical with it. It also appears to be isomeric with *retinylene* from the distillation of resin. It forms a *sulphocymenic* acid.

Lavender oil, $C_{15}H_{14}O_2$ ($=3C_5H_4+2HO$.) This familiar oil is thin, colourless, of density 0.877.

Oil of peppermint from *Mentha piperita* is pale yellow, and lighter than water. It contains a variable proportion of stearopten, so much as sometimes to form a solid prismatic crystalline mass. The composition of the elaopten is $C_{21}H_{10}O_2$; of the stearopten $C_{20}H_{20}O_9$. Phosphoric acid withdraws two atoms of water from the last, and eliminates a liquid hydrocarbon, which M. Walter has named *menthene*, $C_{20}H_{18}$. Distilled with perchloride of phosphorus, the stearopten also gives *chloro-menthene*, $C_{20}H_{17}Cl$. Chlorine is absorbed by the stearopten, and two different chlorinated compounds formed. By the action of nitric acid a liquid acid compound is produced, $C_{10}H_9O_3$. (P. Walter, An. de Chim. lxxii. 83.)

Oil of cedar (*solid*), $C_{32}H_{26}O_2$, or $C_{32}H_{24}+2HO$. The crude essence as obtained from the cedar wood of Virginia is a soft white crystalline mass, which after being deprived of water by heat becomes solid at 80°.6 (27° centig.) Distilled by a sand-pot heat, it comes over between 527 and 572° (275 and 300° centig.), and separates into a crystalline substance and liquid portion. The solid essence, purified by pressure and crystallization from alcohol is remarkable for its beauty and lustre, its odour is aromatic and peculiar, suggesting that of a cedar-wood pencil. It fuses at 165°.2 (74° centig.), and boils at 539°.4 (282°. centig.); it is dissolved very slightly by water, largely by alcohol, from which it precipitates on cooling in silky crystalline needles. The density of its vapour is by experiment 8400; by calculation 8100, allowing its combining measure to be 4 volumes.

When the concrete essence is distilled with anhydrous phosphoric acid, the latter being added in a gradual manner to prevent great elevation of temperature, a liquid is obtained, *cedrene* $C_{32}H_{26}$, which appears to be the hydrocarbon of the essence. Its odour is aromatic and quite peculiar, its density 0.984, its boiling point 478°.4 (248° centig.); the density of its vapour 7900 by experiment, and 7500 by calculation, supposing its combining measure to be 4 volumes. Sulphuric acid and perchloride of phosphorus act upon cedrene as upon menthene. The liquid essence of cedar, obtained from the crude essence by expression, has the same density and composition as cedrene. (P. Walter, An. de Chim. 3 sér. i. 498).

Oil of roses, otto or attar of roses, is colourless, of a most intense rose odour, lighter than water. Its stearopten, which is inodorous, separates at the usual temperature in large plates; it fuses at 95°, is very slightly soluble in alcohol, and contains no oxygen, but is a polymeric variety of CH.

Oil of mentha viridis is, according to the analysis of Dr. Kane, $C_{35}H_{28}O$.

Oil of valerian, extracted from the *Valeriana officinalis*, consists of a hydrocarbon and oxidated oil, the last giving, when treated with potash in fusion, valerianic acid, the same acid as is extracted from the root of valerian, and obtained artificially by the action of potash upon the oil of potatoes.

Oil of chamomile is extracted from the flowers of the *Matricaria chamomilla*; its colour is deep blue. It contains a hydrocarbon and an oxidated oil, the last of which treated with potash in fusion gives valerianic acid. (Gerhardt and Cahours.) The *Anthemis nobilis*, *Arnica montana* and *Archillea millefolium*, yield also blue coloured oils.

Oil of rue, $C_{28}H_{14}O_3$; obtained by distilling fresh plants of the *Ruta graveolens*; is yellowish green, of density 0.837 at 64°.4 (18° centig.); density of vapour by experiment 7892, by calculation 7690, the combining measure being 4 volumes. This oil is soluble in sulphuric acid, and is precipitated by water; hydrochloric acid has no action upon it. (Dr. H. Will in Liebig's Annalen, xxxv. 235).

CAMPHOR.

Formula: $C_{20}H_{16}O_2$, or $C_{20}H_{14}+2HO$. This essence is brought to Europe chiefly from Japan; it is obtained by distilling the wood of the *Laurus camphora* along with water, and is refined by a second sublimation. It is in white translucent crystalline masses, somewhat tough, but easily pulverised when moistened with alcohol; possessing a peculiar taste and smell, and may be obtained in brilliant crystals of a high refracting power, either by sublimation or from solution in alcohol. It floats upon the surface of water, its density being from 0.9857 to 0.997; fuses at 347°, and boils at 399°.2 (204° centig.); the density of its vapour is 5317. It evaporates at the usual temperature, a property that contributes to produce the lively movements which small pieces of camphor exhibit upon the surface of pure water. Like all the essential and fat oils, it also possesses a remarkable tendency to diffuse a thin film of its substance over the surface of water, the result of a kind of capillary attraction, in consequence of which a little column of camphor rising out of water is in the course of a short time cut across at the surface of the liquid. The detaching of the substance of the camphor by this force must occasion a recoil, which appears to be the principal cause of the movements of a floating mass. All movement ceases when a drop of any oil is allowed to fall upon and diffuse over the surface of the water. Camphor is easily kindled, and burns with a white flame. It is but slightly soluble in water, one part of camphor requiring about 1000 parts of water to dissolve it; but the solution has the taste and odour of camphor. It is largely dissolved by alcohol, ether and oils. The solution in proof spirit, known as camphorated spirit, is precipitated by water. Camphor forms liquid compounds with nitric acid, acetic acid and hydrochloric acid. When distilled with anhydrous phosphoric acid it loses 2HO, and yields a pure hydrocarbon, $C_{20}H_{14}$, to which M. Dumas applied the name camphogen.

Camphogen, after being distilled repeatedly from phosphoric acid, is a colourless liquid, of density 0.861 at 57°.2, and boiling at 347°. The density of its vapour is by experiment 4780; by calculation 4697, allowing its combining measure to contain

4 volumes (Delalande.) Camphogen exists in some essential oils, which are mixtures of a liquid hydrocarbon and an oxidated oil, as the essence of cummin. Camphogen in its chemical relations resembles benzin or benzole and napthaline.

Hyposulpho-camphic acid, $HO+C_{10}H_{13}, S_2O_5$; is formed when camphogen is heated on a water-bath with a slight excess of fuming sulphuric acid; the camphogen disappears without any evolution of sulphurous acid, and an acid is produced analogous to hyposulphobenzic acid, which forms a soluble salt with lead. *Hyposulpho-camphate of lead* crystallizes in pearly plates, which contain 4 atoms of water of crystallization, $PbO+C_{20}H_{13},S_2O_5+4HO$; but are made anhydrous by a temperature of 248°. The salt of *barytes* is similar in constitution. This salt and the salt of *lime* are remarkable for their taste, of which the first impression is very disagreeably bitter, but changes in a minute or two into a sweet and sugary taste analogous to that of liquorice.

Camphogen also forms a white crystallizable compound when acted upon by fuming nitric acid. (Delalande, Ann. de Chim. 3 sér. i, 368).

Camphoric acid, $3HO+3C_{10}H_7O_3$. This acid, which is tribasic, is produced by long digestion or repeated distillation of camphor with nitric acid; and is divested of adhering camphor by uniting it with potash, and decomposing the salt by nitric acid. It forms prismatic crystals, which are inodorous, of a very sour taste; fuses at 145°.4 (63° centig.), and emits then a pungent vapour. It sublimes partially as the anhydrous acid. It is indifferently soluble in water, more readily dissolved by alcohol.

Camphoric acid forms a neutral and acid salt with *ammonia*; the former contains 3 atoms of oxide of ammonium, and the latter 2 atoms of the same with 1 atom of water as base.

Acid camphorate of oxide of ethyl is formed when camphoric acid, alcohol and sulphuric acid are heated together; and is separated by the addition of water. It appears to contain a bibasic camphoric acid, of which the formula is $C_{20}H_{14}O_6$, united with 1 atom of oxide of ethyl and 1 atom of water. The atom of water can be replaced by fixed bases, and a class of neutral salts formed. By boiling the acid camphorate of oxide of ethyl with water, it is resolved into tribasic camphoric acid, and *neutral camphorate of oxide of ethyl*, $2EO + C_{20}H_{14}O_6$. (Malaguti).

The matter considered as *anhydrous camphoric acid*, $C_{10}H_7O_3$, is obtained pure by crystallizing in alcohol the product of the distillation of camphoric acid. It forms long flat colourless prisms, which are tasteless and insoluble in water. By continued boiling in water this substance is dissolved, and then appears as the hydrated tribasic acid. (Laurent).

Liquid camphor, $C_{20}H_{16}O$; the elaopten of the *oil of camphor* of commerce. With the same proportions of carbon and hydrogen as solid camphor, it contains only half as much oxygen. The density of the pure oil is 0.91, its boiling point above 212°.

Campholic acid, $HO + C_{20}H_{17}O_3$. The vapour of camphor is entirely absorbed by a dry mixture of hydrate of potash and lime, between 300 and 400° centig., without the disengagement of any gas, and campholate of potash formed. This acid has the consistence of camphor, is insoluble in water, and easily saturates bases; it is camphor plus 2HO. (Delalande, Ann. de Chim. etc. 3 sér. i. 120.) Campholic acid, distilled with anhydrous phosphoric acid yields a hydrocarbon, $C_{18}H_{16}$, =4 volumes of vapour. (Delalande.)

Camphrone, $C_{20}H_{21}O$; was obtained by M. Fremy, by dropping fragments of camphor into a porcelain tube containing quicklime heated to redness. It is a light oil, boiling at 167°, soluble in alcohol and ether but insoluble in water.

C. ESSENTIAL OILS CONTAINING SULPHUR.

Volatile oil of mustard, $C_8H_5NS_2$. Both black and white mustard seeds yield a fat oil by expression. The black seed, when distilled with water, gives a remarkable volatile oil, which is not contained in the seed, but is the result of the reciprocal action of water and an albuminous substance in the seed, named *myrozine* by Bussy, upon another crystallizable principle in it, *myronic acid*, which is soluble in water, and appears to be an acid, although little is known respecting it. This oil is the cause of the acridity of black mustard. The application of boiling water to the mustard, of alcohol, acids or alkalies, which coagulate the albuminous body, prevent the formation of the volatile oil.

This volatile oil is colourless, heavier than water, of a painfully intense odour exciting tears, and produces immediately inflammation and blisters when applied to the skin. Its boiling point is 289°.4 (143° centig.). When burned, it produces sulphurous acid. When the oil and an excess of ammonia are put together in a well stopt phial, the oil in a few days disappears, and a mass of beautiful crystals is found in its place, containing the elements of $C_8H_5NS_2+NH_3$. This compound is believed by MM. Dumas and Pelouze, who examined it, to belong to the class of amides. Oil of mustard is deprived of all its sulphur by distillation with hydrated oxide of lead, ammonia being formed with sulphuret of lead and another crystalline substance, *sinapoline*, $C_{28}H_{24}N_4O_4$, which also remains in the retort. (Simon).

To this class of essential oils also belong, oil of *horseradish*, from Cochlearia armoracia and C. officinalis, oil of *garlic*, from Allium sativum, oil of *onions*, from Allium cepa, oil of *assafœtida*, from Ferula assafœtida, oil of *water pepper*, Polygonum hydropiper, of Arum maculatum; also those of Lepidium latifolium, and of *hops*, Humulus lupulus.

The substances which follow are allied to the essential oils.

Nicotianine, a volatile fatty matter obtained in minute quantity by distilling tobacco leaves with water. It is bitter and has a strong smell of tobacco.

Asarine, from the root of *Asarum Europeum*, a crystalline substance, fusible in boiling water, volatile, having an aromatic smell and taste resembling camphor. Its composition is expressed by $C_{16}H_{11}O_4$ (Blanchet and Sell.)

Anemonine from *Anemone pulsatilla, nemorosa and pratensis*; a crystalline substance, $C_5H_2O_2$ (Fehling); forms anemonic acid with barytes (Lœwig.)

Helenine, from *Inula helenium*; obtained by distilling the fresh root with water, or by acting on it with hot alcohol. It is crystallizable in white prisms, melts at 162°, and boils about 530°. Its formula is $C_{14}H_9O_2$ (Dumas), or $C_{15}H_{10}O_2$ (Gerhardt.) With nitric acid and chlorine it yields two compounds, *nitrohelenine*, $C_{15}H_9O_2+NO_4$, and *chloride of helenine* $C_{15}H_{10}O_2+Cl_2$. With anhydrous phosphoric acid, helenine yields a hydrocarbon $C_{15}H_8$. (Gerhardt, Ann. de Chimie, etc. lxxii, 163.)

The wood of *Quassia amara* contains a crystalline body, so also do the pods of *Epidendron vanilla*, and the seeds of *Tan-*

ghinia madagascariensis, the last highly poisonous, but none of them has been fully investigated.

Caoutchouc, or Indian rubber is the dried milky juice of several trees which grow in South America and the East Indies. The fresh juice was found by Mr. Faraday to contain in 100 parts, 31.7 of caoutchouc, 1.9 of vegetable albumen, a trace of wax, 7.13 of an azotised substance, bitter, soluble of a brown colour in water and alcohol, and precipitable by nitrate of lead, 2.9 of a substance soluble in water, but insoluble in alcohol, and 56.37 parts of water containing in solution a small quantity of a free acid, which precipitated nitrate of lead and coloured persalts of iron green without precipitating them. These substances are dried and included in common caoutchouc, of which the density is 0.9335. Pure caoutchouc carefully prepared from the milk is of density 0.925, transparent and colourless, or of a light yellowish tint in mass. It contains no oxygen, but in 100 parts 87.5 carbon and 12.5 hydrogen, which are nearly in the proportion of C_8H_7 (Faraday).

Caoutchouc is remarkable for its extraordinary elasticity, and its application to remove marks of black lead pencil from paper. It is soluble in pure ether; a small bag of caoutchouc left in common ether for twenty four hours is softened, and may then be greatly expanded by gradually inflating it, so as to become light enough to ascend in the air when filled with hydrogen gas (Mitchell). Caoutchouc when cut into small pieces and well dried at 230°, is dissolved by rectified petroleum, and by the rectified oils from tar; solutions which are extensively used as caoutchouc varnish. Caoutchouc also dissolves in the volatile and fat oils, but loses its elasticity in the latter. Oil of turpentine is often used in the preparation of caoutchouc varnish; to dissolve the caoutchouc, it is said, after it is softened and expanded by the naphtha. To render cloth air and waterproof, Mr. C. Macintosh first applied several coats of this varnish to one side of cotton or woollen cloth, and then bringing the varnished surfaces of two pieces together, passed the double cloth between heavy rollers, by which the two pieces are made to adhere, and the intersticial spaces are completely filled up. The sheet caoutchouc used by chemists is obtained by sawing off a thin slice from a solid block of the material. In forming short connecting tubes of it, the sheet should be folded round the glass tube it is to fit, and the superfluous edges cut close to the glass by sharp scissors; the fresh surfaces being then brought into contact and pressed together adhere perfectly.

Caoutchouc when heated to about 450° enters into fusion and forms a viscid adhesive mass. Distilled at a higher temperature, it yields a fluid product, which is a mixture of several hydrocarbons, differing greatly in volatility, the most volatile boiling at 90°; and the least volatile at 680°. According to Himly, all these volatile oils are of the type C_5H_4, but from their examination by Gregory and by Bouchardat, some of them resemble olefiant gas or C_4H_4. *Caoutchine* of Himly is of one of these liquids, of which the boiling point was constant at 339°. Messrs. Enderby observed that the liquid distilled from caoutchouc is a solvent of that substance.

RESINS.

From their endless variety, these bodies form one of the most extensive and indefinite classes of vegetable principles. Like the resin of turpentine, which may be taken to represent them, they flow from the tree dissolved in essential oils, which are removed by distillation with water. In the liquid or soft state, they are named balsams, which are all compounds or mixtures, like turpentine, of resin and essential oil. There is every reason to suppose a close relation in composition between the oil and its associated resin, the last being often obviously the product of the oxidation of the former. The oxidation of the oil may occur by the combination of the entire oil as a radical with oxygen, or by the oxidation of hydrogen, and its removal from the oil in the form of water, and the replacement of the hydrogen lost by oxygen, in equivalent proportions. The point is not decided by the analytical information we at present possess, but M. Liebig adopting the following composition for:

Oil of turpentine $C_{40}H_{32}$ or $C_{20}H_{16}$

And for:

Resin of turpentine $C_{40}H_{30}O_4$ or $C_{20}H_{15}O_2$,

prefers to represent the oil as the hydruret of a radical, or as

$C_{20}H_{15}+H$, which, like the hydruret of acetyl in olefiant gas is capable of combining directly with hydrochloric acid, and forming a double hydruret, $C_{20}H_{15}+HCl$, or artificial camphor. The same hydruret is converted into the resin of turpentine by the oxidation and replacement of its atom of hydrogen by an atom of oxygen, making $C_{20}H_{15}+O$, and the absorption of an additional atom of oxygen by this compound, making $C_{20}H_{15}O_2$.

Every natural resin is a mixture of several resins, quite as the essential oils are mixtures. They are separated from each other by their unequal solubility in hot or cold alcohol, in ether, in potash and carbonate of potash, or the different solubilities of their compounds with metallic oxides in these and other menstrua. M. Unverdorben, who first threw light on the composition of the natural resins, separated from some, five and more resins, all quite distinct substances. They are heavier than water, and become negatively electrical when rubbed. Some of them which are slightly soluble in water, have a bitter taste, but most of them are quite insoluble in water, and tasteless. They are fusible by a temperature above 212°, and are decomposed by a strong heat. Many resins, when dissolved, redden litmus, combine with bases and possess all the characters of acids; some even decompose alkaline carbonates. Others are neutral, and do not combine with bases. A large number of the resins have been examined and analysed by Professor Johnston, to whose memoirs on the resins contained in the late volumes of the Philosophical Transactions, I must refer for information respecting individual resins.

Amber is found in beds of wood-coal, and appears to be altered resin of the trees. It is a brittle, hard substance, usually nearly transparent, sometimes almost colourless, but commonly yellow or even deep brown, and often includes insects. Its density is 1.065. Amber is insoluble in water, alcohol dissolves about one-eighth of it, refusing to dissolve the rest. Alkalies also act only partially on amber. About 10 per cent of amber is insoluble in ether; what remains dissolves in oil of turpentine and naphtha. Amber thus appears to be a mixture of resins and a bitumen. It contains also succinic acid, which is obtained from it by dry distillation.

RESINOUS VARNISHES.

Varnishes are made by dissolving resins in alcohol, or oil of turpentine, or in a mixture of oil of turpentine and a drying oil. These solutions, when spread upon a surface, evaporate, and leave it covered by a thin coating of the resin. To diminish the brittleness of spirit varnishes, a small quantity of Venice turpentine is added, which gives the coating of varnish a certain tenacity, or a little linseed oil, either alone or mixed with oil of turpentine.

The least coloured varnish is that from copal, which is generally prepared by melting that resin, mixing it while hot with a little drying oil, and adding gradually to the mixture oil of turpentine, in quantity equal to the resin.

Lac varnish or *lacker* applied to articles of brass, is made by heating together:

8 parts of shell lac
4 parts of sandarach
1 part of Venice turpentine
4 parts of pounded glass
60 parts of alcohol.

The use of the pounded glass is simply to assist the solution of the pounded resin by preventing it from agglomerating into a mass, or sticking to the bottom of the vessel. This is an excellent varnish, but has a brown colour.

The varnish usually employed to cover oil paintings, maps and engravings, is made of:

24 parts of mastich
3 parts of Venice turpentine
1 part of camphor
10 parts of pounded glass
72 parts of oil of turpentine

The paper ought to be covered by a solution of isinglass, and dried, before the application of this varnish, which otherwise will sink into the paper, and make it transparent.

GUM RESINS.

Many plants afford a milky juice when cut or pierced, such as the dandelion and poppy, which when exposed to the atmosphere, becomes solid, and assumes different appearances, according to the plant from which it is derived. These concrete juices form the gum-resins, which are important from their applications in medicine. They are essentially mixtures of resins with gum and an essential oil. They form a milky liquid or emulsion with water, the gum only dissolving, while the resin and oil remain in suspension together with various other matters with which they may be accompanied. Alcohol dissolves only a portion of them; but dilute alcohol is their best solvent, as it takes up both the gum and resin. The dilute alkalies dissolve them completely, leaving nothing but foreign matter. In their number are, ammoniac, galbanum, assafœtida, olibanum, myrrh, euphorbium, bdellium, aloes, scammony, gamboge, opium, lactucarium, upas, and many others. Very few of them have much chemical interest, and their treatment properly belongs to pharmacy.

The resinous acids produced by the action of nitric acid on aloes have lately been studied by Mr. E. Schunk; they are remarkable for their splendid red and yellow colours, and form well crystallized salts. They are *chrysolepinic acid*, $HO + C_{12}H_2N_3O_{13}$; *chrysamminic acid*, $HO + C_{15}HN_2O_{12}$; with *alsetinic* and *aloeresinic acids*. (Liebig's Annalen, xxxix. 1.)

CHLOROPHYL.

This name is applied to the green colouring matter of leaves and plants in general, which is observed floating in their cells in the form of green globules. Ether dissolves the colouring matter of these globules, leaving a colourless substance, of which the nature is unknown. Chlorophyl is prepared by digesting fresh green leaves in ether, distilling off the latter, digesting the green residue in alcohol which dissolves it, distilling to dryness, and then digesting the chlorophyl in concentrated hydrochloric acid. The fine emerald green solution in that acid is precipitated by dilution with water. The precipitated chlorophyl is again digested in a concentrated solution of potash, and dissolved by the addition of water. On saturating the last solution after filtration, with acetic acid, chlorophyl precipitates pure, in the condition of beautiful green flocks.

Chlorophyl forms, when dried, a bluish green mass, not fusible, insoluble in water, but dissolving of a fine green colour in alcohol, ether, concentrated sulphuric and hydrochloric acids, and precipitated from these solutions by water. Its solution in alkali is green, precipitated by acids and not by water. Chlorine converts it first into a yellow substance, afterwards into a colourless fatty matter. Chlorophyl is intermediate in its properties between a fat and a resin. Exposed to the light of the sun, it becomes yellow, and is probably then identical with *xanthophyl*, the colouring matter of yellow leaves in autumn.

CLASS II.

CONSTITUENTS OF PARTICULAR PLANTS, OR FAMILIES OF PLANTS.

PIPERIN.

Formula, $C_{34}H_{19}NO_6$ (Regnault).

This is a crystallizable principle in both white and black pepper first observed by M. Oersted; but not the cause of the acrimony of pepper, which is due to a peculiar soft resin. Pepper is exhausted by means of hot alcohol, the solution distilled to the condition of an extract, and that mixed with dilute alkali, by which the acrid resin is taken up, and the piperin left undissolved as a greenish powder, to be purified by repeated crystallization from alcohol.

Piperin forms rhomboidal prisms, of which the angles are 85°.40′ and 94°.20′, colourless, tasteless, inodorous, fusible at 212°, not volatile. It is scarcely soluble in water, and but slightly soluble in alcohol; in cold sulphuric acid it dissolves of a deep red colour.

ASPARAGIN.

Formula, $C_8H_7N_2O_6+2HO$.

A crystallizable substance, first obtained by Vauquelin and Robiquet, in the juice of asparagus; it exists also in potatoes, liquorice root, and particularly in the root of *Althea officinalis*, marsh-mallow, from which last it is generally prepared. The root is exhausted by means of cold water, the solution concentrated by evaporation, and left for a long time in a cool place, for the crystallization of the asparagin. It forms pretty large, colourless, octahedral crystals, of a weak taste, soluble in 58 parts of cold water, insoluble in absolute alcohol, but more soluble in rectified spirits of wine than in water. These crystals lose 12.13 per cent of water at 194°.

Heated with acid or alkaline solutions, asparagin is resolved into ammonia and *aspartic acid,* conducting itself thus like an amide. Heated with water alone, under pressure, above 212°, asparagin is converted into the aspartate of ammonia, by the assumption of 1 atom of water. The formula of anhydrous asparamide is $C_8H_5NO_5+NH_2$.

Aspartic acid, $HO+C_8H_5NO_6$; crystallizes in thin plates, slightly soluble in water, and possessed of weak acid powers.*

SANTONIN.

A crystallizable substance, obtained by Kœhler and by Alms from the seeds of *Artemisia santonica,* or southernwood. It is colourless and destitute of smell, requires between 4 and 500 times its weight of cold, and 250 times its weight of boiling water to dissolve it. It fuses about 276° without loss of weight. The solution of santonin in alcohol reddens litmus, but its acid powers are weak. Its compound with potash, which has been named the *santonate of potash,* is decomposed when its solution is boiled for a few minutes, and the santonin deposited in crystals when the solution cools. It may be combined with other bases, but not without the agency of alcohol. Its analysis gave C_5H_3O, but its atomic weight is supposed to be twelve times as high (Liebig).†

ESCULIN.

This substance is derived, by means of hot alcohol, from the chesnut-tree, ash, and probably other barks. It is in thin colourless plates, or a white powder, of a weak bitter taste, not fusible without decomposition. It is sparingly soluble in cold water. The solution, by exposure to light, acquires a beautiful blue colour, even when the quantity of esculin is very small; the blue tint vanishes with acids, but is revived by alkalies. The composition of esculin is expressed by $C_{16}H_9O_{10}$.

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* Wittstock in Poggendorff's Annalen, xx, 346.

† Tromsdorff Jun.; Liebig's Annalen, xi, 190.

PICROTOXIN.

The substance to which cocculus indicus, the fruit of *Menispermum cocculus*, owes its poisonous qualities, was first investigated by Boullay. It is obtained by boiling in alcohol the bruised seeds, after depriving them, by pressure, of the greater part of their fat oil, distilling off the alcohol, and dissolving the remaining extract in boiling water, slightly acidulated, from which the picrotoxin crystallizes on cooling.

It forms colourless, short and thin prisms, is intensely bitter, and not fusible. It is soluble in 25 parts of boiling water, and very soluble in alcohol; does not combine with acids. It is highly poisonous. Its composition is expressed by $C_{12}H_7O_5$ (Regnault).*

ANTHIARIN.

The most deadly of the Upas poisons, employed by the inhabitants of the East Indian Archipelago to poison their arrows, is a gum resin, from the *Anthiaris toxicaria*, of which the active principle, anthiarim, was separated by MM. Pelletier and Caventou. It crystallizes in fine white plates, which are inodorous, sparingly soluble in water, more so in alcohol. It acts in the highest degree as a deadly poison. Its composition is $C_{14}H_{10}O_5$.

CAFFEIN.

A crystalline substance is obtained from coffee, from tea, and from guarana, a prepared mass from the fruit of *Paullinia sorbilis*. To obtain it from coffee, the raw beans, well dried, are reduced to powder, and exhausted by boiling hot water; subacetate of lead is added to the infusion, to precipitate gum and other matters, the liquid filtered, and the excess of lead thrown down from it by sulphuretted hydrogen. After filtration, the liquid is concentrated by evaporation; the caffein crystallizes on cooling, and is purified by a second crystallization. It may be obtained by boiling tea-leaves in water, filtering and proceeding precisely as with coffee, and also from guarana. It is snow-white, and in fine needles, having a silky lustre, which have a very weak bitter taste; does not act upon vegetable colours, and is sparingly soluble in cold water and alcohol. It loses 8 per cent of water at 212°, fuses at 352° (178° centig.), and sublimes at 725° (385° centig.). From its solution it is precipitated only by tannin. Boiled in a solution of caustic potash, it is resolved into carbonic acid, formic acid and ammonia. With sulphuric acid and hydrochloric acid, it forms crystalline compounds. According to the analysis of Liebig, crystallized caffein consists of $C_8H_5N_2O_2 + HO$. The quantity of this substance in different kinds of coffee was found by MM. Robiquet and Boutron to vary; Martinique coffee containing 6.4 per cent, and St. Domingo coffee only 3.2 per cent of caffein. It is evidently not the principle upon which the peculiar properties of either coffee or tea depend.

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* Pelletier and Couerbe; Ann. de Chim. et de Phys. liv, 181.

Caffeic acid was discovered in coffee by Runge. It is a white powder, which yields, when heated, the characteristic aromatic odour of roasted coffee.

Coumarin is a neutral substance, extracted from the Tonka bean, the fruit of the *Coumarouna odorata*, and the flowers of the melilot, *Melilotus officinalis*, which crystallizes in silky needles, or short prisms. Its composition according to M. Henry is $C_{10}H_3O_2$.

Hesperidin, a crystalline substance, obtained by M. Lebreton from the skin of the unripe orange or lemon.

Populin, found by Braconnot, in the bark of the *Populus tremula*, where it is acompanied by salicin. It crystallizes in snow-white silky needles, has a sweet taste, not unlike that of liquorice, requires about 2000 times its weight of cold water to dissolve it, but dissolves in about 70 times its weight of boiling water.*

Plumbagin, discovered in the root of the *Plumbago europea*.

Daphnin, extracted by Gmelin and Baer from the bark of the *Daphne mezerium*, or common mezerion. It is crystalline, colourless, but little soluble in cold water, soluble in alcohol and ether. Nitric acid converts it into oxalic acid. It is considered by Gmelin and Baer as a body analogous to asparagin.

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* Ann. de Chim. et de Phys. t. 44, p. 296.

VEGETABLE ALBUMEN AND LEGUMIN.

When fresh gluten from wheaten flower is digested in hot alcohol, till everything soluble is taken up, *vegetable albumen* is left, of a greyish colour. It is soluble in water, and is coagulated by heat, insoluble in alcohol and ether, and agrees perfectly in properties with animal albumen.

Braconnot observed a peculiar principle in the fleshy cotyledons of the seeds of papilionaceous plants, to which he gave the name *legumin*. Ripe peas, softened with water and reduced to a pulp, gave, when mixed with pure water, a milky liquid, from which starch precipitated, and which retained legumin in solution, seemingly combined with a vegetable acid. When evaporated by heat, the solution does not coagulate, but deposits the legumin by little and little, under the form of diaphanous pellicles. It is purified by washing it, while still moist, with boiling alcohol. It then has a fine white colour, and does not affect litmus paper. Legumin is soluble in water, but insoluble in alcohol. It dissolves very readily in acetic, oxalic, citric and other vegetable acids, but is precipitated from solution, on the contrary, by the mineral acids, which last, form sparingly soluble compounds with legumin. Alkaline hydrates and carbonates also dissolve it with facility, and the solutions froth like a soap.

M. Liebig has lately made the interesting observation that legumin is identical in properties with the animal principle *casein*, and has the same composition. It is also accompanied by the same salts, namely potash, phosphate of potash, magnesia, lime and oxide of iron, as the casein of milk.

NEUTRAL COLOURING MATTERS.

INDIGO.

Formula of blue indigo, $C_{16}H_5NO_2$. (Crum, Dumas).

This important colouring matter exists in the leaves of all the species of the *Indigofera*. It is obtained also from *Nerium tinctorium*, and in small quantity from *Isatis tinctoria* (pastel or woad), and various other plants. In India, the indigofera plants are cut before flowering, and allowed to steep for nine or twelve hours in a vat, covered with water, in which fermentation occurs with the evolution of carbonic acid and hydrogen gas. A yellow coloured liquor is drawn off into another vat, in which it is beat and stirred till it acquires a blue colour, and the indigo precipitates. It is then drained on calico, placed on proper frames, and strongly pressed by means of screws, cut into cakes of the proper size, and dried.* The plant thus appears to contain the indigo in a very different state from that in which it is ultimately obtained. It is not certain that it can be extracted from the indigofera without fermentation; but Chevreul has shown that it may be extracted from pastel, by treating the latter with hot water free from oxygen, and that the yellow solution thus obtained became blue, and deposited indigo.

The indigo of commerce is of a deep blue, inclining to black; its fracture is earthy and dull, but becomes of a coppery red when rubbed with a hard body, and the more brilliant and like copper the colour developed by friction, the purer is the indigo considered. It is far from being a pure substance, rarely containing half its weight of blue colouring matter, and often much less. Berzelius separated from it; 1, *gluten of indigo*, by digesting indigo in fine powder with a dilute acid, which also dissolves some salts of lime and magnesia; 2, a principle which he has named *indigo brown*, by means of a concentrated solution of caustic potash gently heated; and 3, *indigo red*, by afterwards boiling the indigo repeatedly with alcohol of density 0.830. Indigo blue remains, but is not yet absolutely free from foreign matter.

To obtain it pure, recourse is had to the solution of indigo in the ordinary indigo vat, or the indigo purified by the preceding processes may be dissolved by imitating on a small scale the preparation of the dyer. One part of indigo in an impalpable powder and 2 parts of quick-lime, recently slaked, are mixed, and introduced into a well stopt bottle with about 150 parts of water. To this is then added two thirds of the weight of the lime of crystallized protosulphate of iron in fine powder, or dissolved in a small quantity of hot water. The bottle then being completely full and well closed, is agitated occasionally for several hours, and kept in a warm place till the supernatant liquor acquires a yellow colour. The protoxide of iron precipitated by the lime becomes peroxide, taking oxygen from the blue indigo, which in this altered state forms a compound with the lime, soluble in water. When the yellow solution of this compound is poured out or exposed to air, it rapidly becomes blue from the absorption of oxygen, the indigo loses its solubility and precipitates. In the usual process of dyeing, the indigo is fixed by dipping the yarn or cloth in the same solution of indigo, and then exposing it to air; the indigo thus penetrates into the cloth in a soluble state, and is rendered insoluble afterwards by oxidation within its substance, so that it cannot afterwards be washed out. The sediment in the bottle yields more soluble indigo, when agitated again with pure water slightly heated, or with lime-water. The yellow solutions are mixed together and freely exposed to air, with the addition of a little hydrochloric acid to dissolve the salts of lime, and the blue indigo which precipitates is collected, washed upon a filter and dried. It is afterwards washed with boiling alcohol by M. Dumas to take up the *indigo red* of Berzelius.

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* Dr. Thomson's Organic Chemistry, Vegetables, p. 369.

The purified indigo, when dry, is of a deep blue, with a shade of violet, and when rubbed, exhibits a strong copper red colour and metallic lustre. It is tasteless, inodorous, insoluble in water, alcohol, ether, and not affected by alkalies or diluted acids. When heated to about 550°, it fuses (Crum), and at the same time emits a beautiful purple red vapour and sublimes, condensing in small copper-coloured prisms, but it is always partially decomposed at the same time. To observe the beautiful appearance of sublimed indigo, ten or twenty grains of good indigo in powder may be put upon a pretty thick sheet of iron or copper, pressed flat and then covered by the lid of a platinum or porcelain crucible, two or three inches in diameter, while the plate is heated sharply by placing it over a lamp or choffer. On raising the cover, after the plate is cool, the charred mass will be found entirely covered by copper-coloured crystals. Their density is 1.35. Blue indigo was carefully analysed by Mr. Crum,* and repeatedly by M. Dumas, whose results confirm the original determination of Mr. Crum.†

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* Thomson's Annals of Philosophy, second series, v. 82.

† Dumas, Ann. de Chim. et de Phys. t. 73, p. 269; and 3 sér. t. 2, p. 204.

White or *reduced indigo* is produced by the action upon blue indigo of deoxidating bodies of all kinds, such as the protoxides of iron and tin, sulphites and phosphites and many sulphurets, particularly the sulphuret of arsenic or orpiment, but only with the concurrence of an alkali or alkaline earth, which may combine with the reduced indigo. On neutralising a solution of the alkaline compound with hydrochloric acid, carefully excluding air, the reduced indigo is thrown down as a white precipitate, flocculent, and composed of minute crystalline plates. Carefully dried in vacuo, it is coherent, of a greyish white colour and silky lustre; in the dry state it soon becomes blue superficially in the air, but requires several days to become entirely blue. When humid or dry, it is tasteless, inodorous, insoluble in water, soluble in alcohol and ether, which it colours yellow; but it is soon deposited from the alcoholic solution as blue indigo, when exposed to air. White indigo does not affect litmus, dissolves in alkalies without neutralising them, and has not marked acid characters, although it combines with bases. According to the observations of Dumas, the conversion of white into blue indigo occurs in air without any change of weight, or there is, at the utmost a slight but sensible loss.

White indigo was named *indigogen* by Liebig, and blue indigo considered the oxide of that radical. M. Dumas takes another view of the relation between these bodies, considering white indigo not as deoxidised blue indigo, but blue indigo combined with an atom of hydrogen, and forming a hydruret, analogous to the hydruret of benzoyl, thus:

White indigo . $C_{16}H_5NO_2$.
Blue indigo . . $C_{16}H_5NO_2+H$.

In the oxidation of indigo, on this view, water is formed and liberated. M. Dumas still adheres to this view in his late Memoir on indigo. The combustion of white indigo he found to be easily affected, but that of blue indigo is attended with difficulty, so as to leave some uncertainty as to its composition. According to M. Erdmann, the formula of blue indigo is $C_{32}H_{10}N_2O_3$.

Action of sulphuric acid.—Indigo combines with fuming sulphuric acid or oil of vitriol, when slightly heated with that acid in the proportion of 1 to 8, without any evolution of sulphurous acid, and forms a semi-fluid mass, popularly known as *sulphate of indigo*, which dissolves in a considerable quantity of water, of an intense blue colour. The products of this action were first examined by Mr. Crum, whose results form the basis of M. Dumas' later investigations. To convert blue indigo into *sulphindylic acid*, the latter chemist recommends the digestion of the indigo in a large quantity, not less than 15 parts, of concentrated oil of vitriol, for three days in a bath maintained at a temperature of 120° or 140°. The solution is afterwards diluted with water and filtered, although when these precautions are attended to, little or nothing insoluble remains on the filter. To the limpid liquid a strong solution of pure acetate of potash is added, and the precipitate which falls is washed with acetate of potash, in which salt the sulphindylate of potash is insoluble although soluble in water; the acetate of potash remaining in the precipitate is got rid of by diffusing the latter through a quantity of ordinary alcohol and filtering again. The blue matter remaining when well dried at 212°, gave by analysis, $KO+C_{16}H_4NO,S_2O_6$; conducting to the following formula for hydrated sulphindylic acid, $HO+C_{16}H_4NO,S_2O_6$. Blue indigo thus appears to lose HO in the formation of sulphindylic acid. *Sulphopurpuric acid*, remains upon the filter in the preparation of sulphate of indigo, when 8 or 10 parts only of sulphuric acid have been employed to 1 of indigo. It is drained, and washed with diluted hydrochloric acid, till the washings are colourless and free from sulphuric acid. It is then carefully dried about 392° (200° centig.). This purple acid gave by analysis, $C_{32}H_{10}N_2O_4+2SO_3$. The sulphopurpurate of potash is obtained by dissolving the acid in water, and adding acetate of potash to the liquid; it precipitates in purple flocks, which should be washed first with a solution of acetate of potash, and then with alcohol. Its composition indicates that the atom of indigo $C_{16}H_5NO_2$ takes the isomeric state $C_{32}H_{10}NO_4$, to constitute sulphopurpuric acid. M. Dumas institutes the following comparison between the indigo and benzoyl compounds:

$C_{16}H_5NO_2$	Blue indigo	$C_{14}H_5O_2$	Benzoyl
$C_{16}H_5NO_2,H$	White indigo	$C_{14}H_5O_2,H$	Essence of bitter almonds
$C_{16}H_5NO_4$	Isatin of Laurent	$C_{14}H_5O_4$	Salicyl
		$C_{14}H_5O_4,H$	Hydruret of salicyl.

Action of fused potash on indigo.—M. Gerhardt has made the curious observation that when blue indigo is thrown in small portions into fused hydrate of potash, that body dissolves losing its colour, disengaging abundance of hydrogen and ammoniacal gas, and leaving as a fixed residue a mixture of valerate and carbonate of potash. The reaction takes place at the expense of the elements of water; 1 atom of indigo with 14 atoms of water giving 1 atom of valerianic acid, 6 atoms of carbonic acid, 1 atom of ammonia and 6 atoms of hydrogen. On heating the saline residue slightly with sulphuric acid, valerianic acid is obtained in large quantity. This indeed appears to be the most eligible process for preparing that acid.

Indigo is much used in dyeing, being principally applied in the deoxidised state, and forms one of the most permanent colours, resisting every thing except chlorine and nitric acid. In the form of sulphate of indigo, it is used for Saxon blue, which is much less permanent.

Anilic or indigotic acid, $HO+C_{14}H_4NO_9$ (Dumas); is formed when indigo is dissolved in nitric acid considerably diluted, and may be crystallized by concentration of the liquid. It forms colourless prisms, of a sourish bitter taste, fusible and volatile, sparingly soluble in water. It forms crystallizable salts, which detonate feebly when heated. The formula of the salt of silver is $AgO+C_{14}H_4NO_9$ (Dumas). The indigo therefore in forming anilic acid with nitric acid, loses 2 atoms of carbon and 1 of hydrogen.

Picric acid, carbazotic acid, $HO+C_{12}H_2N_3O_{13}$ (Dumas). This acid, which was first known as the *bitter of Welter*, is produced by the action of nitric acid on the preceding compound, and by the solution of indigo or any other azotised organic substance in concentrated nitric acid. It crystallizes in yellow brilliant prisms, of a very bitter taste, which are fusible and volatile, and burn with flame when sharply heated; they are sparingly soluble in water, which they colour yellow. Picric acid is not decomposed by other acids nor by chlorine. Its salts are yellow and generally crystalline; they detonate strongly when sharply heated, or sometimes by a blow, particularly the potash salt. M. Piria has also observed the formation of picric acid in the treatment of hydruret of salicyl with nitric acid.

Chlorisatin, $C_{32}H_4NClO_3$.* When chlorine gas is transmitted through water in which blue indigo is suspended, hydrochloric acid is formed, and the indigo is converted into a reddish yellow matter, which Erdmann has found to be a mixture of several new products, of which the most remarkable are two chlorine compounds, which have been named chlorisatin and bichlorisatin. When the yellow matter is digested in boiling water, a resin is left undissolved, and a solution formed, which on cooling, deposits a reddish yellow crystalline powder, which is a mixture of the two compounds mentioned. When this is dissolved in boiling alcohol, the chlorisatin crystallizes out first. It forms orange-yellow, four-sided prisms, is bitter, soluble in alcohol, but highly insoluble in cold water. It is partially decomposed by sublimation.

Chlorisatin dissolves in a solution of caustic potash, of a red colour. When heated, the colour of this solution changes to yellow, and a potash salt crystallizes on cooling, in shining plates, of which the composition is $KO+C_{32}H_5NClO_4$. It contains *chlorisatinic acid*, into which, under the influence of bases, chlorisatin is converted, by the fixation of the elements of an atom of water. Strong acids throw down chlorisatin again from the potash salt. The salt of *lead* is a yellow precipitate, which becomes of a fine scarlet on standing. The salt of *copper* is thrown down brownish yellow, but becomes blood-red and granular.

Bichlorisatin, $C_{32}H_4NCl_2O_3$; contains twice as much chlorine as chlorisatin, but greatly resembles it in properties, and is analogous in its relation to alkalies. The salt of lead of its acid is permanently yellow; the copper salt, which first appears as a brown gelatinous precipitate, soon becomes greenish yellow, and then of a splendid blood-red and granular. It is said to form a very fine red on drying, and to take a gold lustre by friction.

Chlorisatyde, $C_{32}H_5NClO_3$; a white substance, which is formed when sulphuretted hydrogen is sent through a solution of chlorisatin in alcohol; the liquid becomes colourless, and sulphur is precipitated at the same time. Bichlorisatin in similar circumstances yields *bichlorisatyde*, $C_{32}H_5NCl_2O_3$. When treated with potash chlorisatyde and bichlorisatyde yield *chlorisatydic* and *bichlorisatydic acids*.

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* So named from *Isatis tinctoria*. These formulæ are to be considered with reference to the formula ascribed to blue indigo, by M. Erdmann, namely $C_{32}H_{10}N_2O_2$.

Chloranile, $C_6Cl_2O_2$, one of the products of the continued action of chlorine upon chlorisatin and bichlorisatin dissolved in alcohol. It is a volatile substance in crystalline scales of a brass yellow colour, which is dissolved by potash of a purple colour, but is then converted into chloride of potassium and chloranilate of potash. *Chloranilic acid* is a reddish powder, composed of fine scales; its composition is C_6ClO_3.

Chrysanilic Acid, $HO+C_{28}H_{10}N_2O_5$. When indigo in powder is added to a solution of caustic potash, of density 1.35, and boiled in a silver vessel, an orange-yellow salt is formed, without any evolution of gas. The acid is separated as a reddish-brown precipitate on the addition of sulphuric acid to a solution of the potash salt; it is named chrysanilic acid, from its relation to aniline and the golden-yellow colour of its salts. (Fritsche).

Anthranilic Acid, $HO+C_{14}H_6NO_3$. The solution of the fused mass above becomes blue in the air from absorption of oxygen, like a solution of white indigo, and blue indigo precipitates in crystalline grains. On boiling the solution with dilute sulphuric acid, the decomposition proceeds more rapidly, and a brown resinous mass is obtained, soluble in alcohol, ether, and alkalies. To prepare this acid, the first alkaline solution is diluted, and peroxide of manganese added to it in small quantities, at the boiling point, till the solution gives no black precipitate when rendered acid, and its colour is not reddish-brown but a dirty greyish brown. This acid, when sublimed, is white, and resembles benzoic acid, but the fused sublimate is yellow. Its salt of *lime* is very soluble in hot water, and crystallizes in colourless rhombohedrons. Anthranilic acid, distilled by the heat of a spirit lamp, is decomposed in a considerable measure, and resolved into carbonic acid and aniline. (Fritsche; Liebig, Annalen, &c., xxxix. 76 and 91.)

Aniline, $C_{12}H_7N$ (Fritsche); an oily liquid, which distils over when finely pulverised indigo is decomposed by a highly concentrated solution of caustic potash or soda in a retort. Its quantity amounts to about 18 or 20 per cent of the indigo employed. The density of aniline is 1.028, it boils at 442°.4 (228° centig.). Its smell is strongly aromatic, but at the same time disagreeable, it is sparingly soluble in water, but mixes in all proportions with alcohol and ether. Exposed to the air, it acquires a yellow colour, and becomes resinous. The most remarkable property of aniline, is its basic character. It forms salts with acids, assuming an atom of water when it unites with oxygen acids, and combining directly with hydracids, exactly like the vegeto-alkalies and ammonia.

Oxalate of aniline is formed by mingling together alcoholic solutions of aniline and oxalic acid; it falls as a white powder, which is to be washed with alcohol, from which it crystallizes on cooling. Its formula is $C_{12}H_7N+HO,C_2O_3$. *Hydrochlorate* of aniline is prepared by mixing aniline with hydrochloric acid, and crystallizing the salt; it dissolves easily in water; its formula is $C_{12}H_7N+HCl$.*

Unverdorben had previously obtained, among the empyreumatic products of the dry distillation of indigo, an oily alkaline body, which he had distinguished as *crystalline*, because it has the property of forming crystallizable salts with acids. It was not analysed, but there can be little doubt that it is identical with aniline.

COLOURING PRINCIPLES OF ARCHIL, LITMUS, AND CUDBEAR.

Various lichens, which communicate no colour to pure water, strike a fine blue with solution of ammonia. They contain certain crystallizable principles, in themselves colourless, which are thus modified by assuming the elements of ammonia. The history of these principles is still incomplete, although considerable progress has been made in their investigation by the labours of Robiquet, Heeren, Dumas, Kane, and E. Schunk. The limits of this work will not permit me to enter into details respecting the various bodies obtained, of which I can do little more than indicate the names and the composition when determined.

From archil weed, the *Roccella tinctoria*, Dr. Kane obtained the following series of substances, either existing in the lichen, or produced by the action of re-agents upon principles existing in it.

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* Fritsche in Liebig's Annalen, xxxvi, 84.

1. *Erythrilin*, $C_{32}H_{16}O_6$; a white powder, insoluble in water, but converted by ebullition into erythrilin bitter, soluble in alcohol and ether, also in alkaline liquids, from which it is precipitated by an acid; not volatile.

2. *Erythrin*, $C_{20}H_{13}O_9$; sparingly soluble in cold water, but very soluble in boiling water, and separating on cooling in brilliant, micaceous, snow-white scales; the solution is colourless, but in air becomes rapidly brown, and is decomposed. It is very soluble in alcohol, ether and alkaline solutions, from which it is precipitated unaltered by an acid. It fuses at 220° without losing water, and is decomposed at a higher temperature without volatilising. This substance agrees in composition and properties, and is believed by Dr. Kane to be identical with the *pseudo-erythrin* of Heeren, derived from the *Parmelia roccella*. It forms a wine-red solution when exposed to the conjoint action of ammonia and air.

Erythrin bitter, amarythrin, $C_{22}H_{13}O_{14}$; is formed when erythrin is dissolved in hot water and exposed some days to the action of air. It is a bitter extractive matter, very soluble in water, much less so in alcohol, and not at all in ether. It is precipitated, like the preceding compounds, by a salt of lead. This is the erythrin bitter of Heeren.

4. *Telerytrin*, $C_{22}H_9O_{18}$; formed when amarythrin, in a semi-fluid state is exposed for several months to air, the latter changing gradually into a mass of very minute granular crystals, of a brownish yellow colour, but becoming white when purified by crystallization from alcohol.

The ordinary *archil* (orseille) of commerce is prepared from the *Parmelia* or *Roccella*. The lichens are reduced to a pulp, and treated with impure ammoniacal liquors. The complete production of archil requires a considerable time, and from Dr. Kane's observations, the colouring matter is in a constant state of transition.

Orcin (cr.), $C_{18}H_{12}O_8$; a colourless crystallizable substance, obtained by Robiquet from the *Lichen dealbatus*. The dried lichen is boiled with alcohol, the solution filtered hot, and distilled to the condition of an extract; the last is exhausted by water, and the concentrated solution brought by evaporation to a state for crystallization. The orcin is purified by treatment with animal charcoal and repeated crystallization. It forms colourless, four-sided prisms, of a sweet but disagreeable taste, soluble in water and alcohol, easily fused and volatile. Its most characteristic property is the becoming of a deep violet colour, when exposed to the joint action of ammonia and air, owing to the formation of *orcein*. Orcin forms a compound with oxide of lead, of which the formula is $C_{18}H_7O_3+5PbO$.

Orcein.—The orcein of archil is of a fine red colour, slightly soluble in water, but colouring it strongly, and wholly precipitated from it by the addition of a neutral salt. It is very soluble in alcohol, which it colours scarlet, and from which water precipitates it. It is scarcely soluble in ether. Orcein dissolves easily in potash or ammonia, giving it a magnificent purple colour, the colour of ordinary archil; from this solution, the colouring matter may be separated by the addition of an excess of common salt. An alkaline orceinate gives with metallic salts, lakes of a fine purple of different shades, which, however, lose much of their lustre in drying. Dr. Kane finds the orcein of archil to be often a mixture of two substances, differing in their proportion with the age of the archil, which he names *alpha-orcein* and *beta-orcein*; the last is produced by the oxidation of the first, and is the orcein of Robiquet and other chemists. Their formulæ are:

Alpha-orcein . .	$C_{18}H_{10}NO_5$	(Kane).
Beta-orcein . .	$C_{18}H_{10}NO_8$	(Liebig, Kane).

The last was dried before analysis at 212°. The formulæ of their compounds with oxide of lead are: that of alpha-orcein, $C_{18}H_{10}NO_5+3PbO$, and that of beta-orcein, $C_{18}H_{10}NO_8+3PbO$. The two orceins are identical in all their essential chemical properties; have the same solubility in water, alcohol and ether. The formula of anhydrous orcin being $C_{18}H_7O_3$, that substance requires only to combine with 1 atom of ammonia, together with 2 or 5 atoms of oxygen, to form the one or other variety of orcein.

In addition to the two orceins, the archil of commerce contains *erythroleic acid* and *azoerythrin*, of which the former admits of two modifications; besides the *yellow matter* of Heeren.

Azoerythrin consists of $C_{22}H_{19}O_{22}$ (Kane), by abandoning 4 atoms of carbonic acid and 9 atoms of water, it will yield an equivalent of alpha-orcein.

Erythroleic acid, $C_{26}H_{22}O_8$ (Kane), is a purple substance, distinguished for its semi-fluid consistence at the ordinary temperature, and its solubility in ether and alcohol.

Rocceilic acid, $C_{16}H_{16}O_4$ (Liebig), one of the principles extracted by Heeren.

Litmus.—The cubical masses of commercial litmus being reduced to powder and treated with boiling water give a deep blue solution. The mass of insoluble matter, which is of a paler blue than the original substance, is diffused through water and reddened with hydrochloric acid. The whole is then thrown upon a filter, and the red insoluble substance which remains is washed with water until all excess of hydrochloric acid is removed and then carefully dried. The mass when completely dry is boiled in successive portions of alcohol, until every thing soluble in that liquid is taken up. The deep red alcoholic liquors are then distilled in a water-bath to dryness, and the resulting solid material digested in warm sulphuric ether until the latter no longer becomes coloured. The ethereal solutions thus obtained, yield on distillation in a water-bath a fine crimson oily material which is nearly fluid. When purified, this matter forms *erythrolein,* $C_{26}H_{22}O_4$. This compound is completely liquid at 100°; its solutions in alcohol and ether are of a fine red colour, and it tinges water pink, without however dissolving in any very sensible proportion.

The substance from which the erythrolein has been removed, and which is distinguished by its solubility is *erythrolitmin,* $C_{26}H_{22}O_{12}+HO$; it is of a bright red colour, sparingly soluble in water, which it colours red. It dissolves of a blue colour in potash, and combines with ammonia.

The brownish red mass which resisted the action of alcohol, yields its colouring material but very sparingly to water also; but it may be dissolved in a large quantity of boiling water, and gives by evaporation a deep blood-red mass, consisting of pure colouring material, which has been named *azolitmin,* $C_{18}H_{10}NO_{10}$; it differs only from alphaorcein and betaorcein in the proportion of oxygen it contains.

Another substance occasionally but rarely present in litmus is *spaniolitmin* $C_{18}H_7O_{16}$. It is of a bright red colour, insoluble in alcohol and in ether, and very sparingly soluble in water, which it tinges bright red.

The blue liquors which are obtained in the first place by digesting litmus cakes in water contain but a small quantity of colouring matter, considering their depth of tint. It is generally azolitmin nearly pure; with occasionally a small portion of spaniolitmin.

By the action of chlorine upon orcein, *chlororcein* is formed, $C_{18}H_{10}NO_8,Cl$, which possesses a yellowish brown colour. With azolitmin a similar compound of chlorine is produced, $C_{18}H_{10}NO_{10},Cl$. By the action of nascent hydrogen upon orcein, a colourless body is formed, *leucorcein*, $C_{18}H_{10}NO_8,H$. For all these facts we are indebted to Dr. Kane (Phil. Trans. 1840, p. 298).

Cudbear, in German *persio*, is prepared from the *Leconora tartarea*, *Parmelia omphalodes*, and probably other lichens. The lichen is steeped and left for some time in open vessels covered by ammonia, till the purple colour is sufficiently developed, and then the whole is dried in the open air and reduced to a fine powder.

Mr. Schunk has lately obtained by extraction with ether from the *Leconora tartarea* and other lichens employed in the manufacture of cudbear a white crystalline substance *leconorin*, which is dissolved by alkalies and precipitated again unaltered by acids. But if the alkaline solution is allowed to stand for an hour, no precipitate is afterwards obtained, the new substance having resolved itself into carbonic acid and *orcin*. When the solution of the new substance in barytes-water is heated to the boiling point, carbonate of barytes precipitates and the solution yields by evaporation large crystals of orcin. It is probable therefore that orcin does not exist ready formed in any lichen, but is always the product of the action of an alkali, a circumstance which has hitherto been overlooked.

Litmus is much used as a re-agent from its susceptibility to the action of acids and alkalies, being reddened by the former and having its blue colour restored by the latter. In preparing litmus paper an infusion is made of commercial litmus, filtered, concentrated by a water bath, and a very small quantity of carbonate of soda added. Good letter paper cut into slips of three inches in breadth is dipt into the infusion, allowed to dry and the dipping repeated; or the infusion may be applied to one side only of thin and sized drawing paper. For red paper, the infusion of litmus is acidulated slightly by means of acetic acid. A paper prepared from an infusion of the best cudbear without the addition of either alkali or acid has a purple colour and is affected by both acids and alkalies. It is convenient in alkalimetry, being already too red to be sensibly affected by carbonic acid, while it is distinctly reddened by the mineral acids. The colours from the lichens are beautiful, but fugitive; they are chiefly employed by the dyer to give a bloom to more fixed colours.

COLOURING MATTERS OF MADDER.

Alizarin,* $C_{37}H_{12}O_{10}$ (Robiquet).—This is a crystalline matter of a red colour which was extracted by MM. Robiquet and Colin from the ground roots of madder, the *Rubia tinctorum*. To concentrated sulphuric acid an equal quantity of ground madder is added in a gradual manner, so as to prevent any sensible elevation of temperature; in two or three days nearly all the constituents of the madder are charred and destroyed except the alizarin. The acid is then washed out from the black mass, which is dried and digested with portions of cold alcohol, to take up a fatty matter it contains. The alizarin is afterwards dissolved out by boiling alcohol, the latter solution mixed with water, the alcohol distilled off, and the alizarin which has precipitated is collected on a filter.† It is a red powder, which may be sublimed and is obtained in long flexible capillary needles, having an orange colour; but unless the subliming vessels be very low and flat, almost the whole of the alizarin is decomposed. Alizarin is somewhat soluble in boiling water to which it communicates a rose colour; at 54°, it dissolves in 212 parts of alcohol and in 160 parts of ether. It has a decided affinity for some animal matters, being soluble in albumen, and is precipitated in combination with the latter when coagulated. Phosphate of lime appears also to combine with the colouring matter of madder, from the well known fact that the bones of animals which have taken for some time madder mixed with their food, are tinged red.

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* From *alizari* the name applied to madder roots in the Levant.

† Annales de Chimie et de Physique, tome 34, p. 228; and Journal de Pharmacie, tome 21, p. 392.

The colouring matter of madder has also been examined by Gaultier de Claubry and Persoz,* by H. Schlomberger,† and by Dr. F. Runge.‡ From their inquiries it is certain that alizarin is not the only or perhaps even the most important colouring matter of madder. These different inquirers have extracted various substances from madder, but do not agree in the mode of representing its constitution; as the purity however of these substances was not tested by analysis, their definite character is necessarily very doubtful. I can only enumerate here the different colouring matters extracted from madder by Dr. Runge. They are (1) *Madder purple*, dissolved out from madder, previously well washed with water between 56 and 70°, by a strong boiling solution of alum, and precipitated from the alum solution by the addition of sulphuric acid. When purified it is a light crystalline powder of a beautiful orange-yellow colour. When used in excess it imparts to cotton impregnated with the alum mordant, a deep reddish brown purple colour; but if on the contrary the cotton be in excess, the colour is bright red. (2) *Madder red*, the alizarin of Robiquet and Colin, which according to Runge may be sublimed a second time without decomposition. It may be separated from madder purple, in consequence of its insolubility in a strong solution of alum. (3) *Madder orange*, which is distinguished and separated from the two former, by its little solubility in spirits. When in excess it imparts to alumed cotton a bright orange colour. If water be added to a hot solution of it in spirit, small crystals separate, as with madder-red and madder-purple under the same circumstances. (4) *Madder yellow* is remarkable for its great solubility in water and its little affinity for cloth impregnated with alum. It abounds in Dutch madder. (5) *Madder brown*, another principle, which like the last has no value as a dye stuff.

The most fast and brilliant reds are obtained upon cotton by means of madder, as also an equally stable and valuable purple;

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* Ann. de Chim. et de Phys., t. 48, 72.

† Bulletins of the Industrial Society of Mulhausen.

‡ Dr. R. D. Thomson's Records of Science, vol. 2, p. 452, and vol. 3, pp 44 and 135.

the first are known as Adrianople or Turkey reds. The colouring principles of madder have an affinity for the earth alumina and peroxides of iron and tin, like other organic colouring matters soluble in water, and form insoluble precipitates with these oxides, which are known as *lakes*. By impregnating cotton cloth with a solution of acetate of alumina, or with alum of which the acid has been in a great measure neutralised by an alkali, it retains a portion of that earth, (or of either the other metallic oxides mentioned if treated with a solution of their salts), of which it is not deprived by washing; these oxides having an attraction or affinity for the fibre of the cotton. If the cloth so prepared be introduced into a hot solution of any organic colouring matter, the latter is taken up from the solution and becomes attached to the cloth by combining with its alumina, which thus forms the link that unites the cloth and colouring matter. The alumina is termed the mordant, and such is the ordinary method of fixing colours by means of mordants. Cotton may be dyed with madder by this simple process, but the colour is dull. To produce a fine red the cloth must be submitted to a long preparation occupying some weeks, and consisting of a number of operations, the effect of many of which is very imperfectly understood, but every one of them nevertheless indispensable for a good result. The chief features of this remarkable process, without entering into a detail of the routine operations are (1) the impregnation of the cloth with an imperfect soap and some principles from sheeps' dung. By this treatment, which consists of several operations repeated more than once, the cloth acquires an animal odour, which it retains through the rest of the operations. It is said that when old cotton cloth that has been worn about the person and frequently washed is to be dyed, this process may be omitted altogether. (2) The cloth is afterwards soaked in an infusion of vegetables or of sumach, which gives it a yellow colour and assists also in fixing the madder afterwards, this is the *galling*, an accessory operation not confined to madder dyeing. (3) Alumina is fixed in the cloth in the manner previously described. (4) The cloth is then dyed by entering it into a boiler with ground or chopped madder while the water is cold, gradually raising the temperature, and boiling them together for a couple of hours. A certain quantity of bullock's blood is also added to the madder bath. The colour thus fixed is brownish red and dull, owing to the *Madder brown* being fixed in the cloth, as well as the madder purple and madder red. The object of (5) *the clearing process* is to get rid of the brown which is not nearly so fixed as the red. It consists of boiling the cloth in alkali and soap; afterwards with soap and protochloride of tin under a pressure of two atmospheres, and finally exposing the cloth on the grass to the sun for a few days.

If the cloth be prepared and dyed with madder in the same manner, with the exception of charging it with an iron instead of an aluminous mordant, it is dyed of a beautiful and permanent purple, instead of red.*

CARTHAMIN.

Safflower consists of the flowers of *Carthamus tinctorius*; it contains two colouring matters, a yellow, which is of no value, and a beautiful but fugitive red used in silk dyeing, which is named carthamin or carthamic acid. The yellow matter is soluble in water, the red insoluble in water but soluble in alkalies. They are separated by adding an acid to an alkaline infusion of safflower, which throws down the carthamin, and afterwards passing clean cotton yarn through the liquid; in these circumstances, the yarn takes up the carthamin entirely and is then washed with water. The pure carthamin is afterwards stript from the cotton by an alkali and the solution is employed to dye silk by acidulating with citric acid, and then passing the silk through the liquid in the usual way by means of a winch.

The pigment *rouge* contains precipitated carthamin intimately mixed with finely divided talc.

According to Doebereiner, carthamin has an acid reaction; it is but slightly soluble in alcohol or ether. Soda saturated with carthamin is said to crystallize in fine colourless needles having a silky lustre, and becoming instantly red when an acid is added.

HEMATOXYLIN.

This is the colouring matter of logwood, the wood of the *Hæmatoxylon campeachianum*; it was named *Hematin* by

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* An outline of the process of Turkey red dyeing as practised at Glasgow is given by Dr. Thomson, in his Organic Chemistry, Vegetables, p. 396. For this and other dyeing processes, see also Leuch's *Traité complet des Matières Tinctoriales.*

M. Chevreul,* who first distinguished it. It is sometimes so abundant as to exist in the wood in large crystals. The rasped or chopped wood is exhausted by means of water of a temperature between 122° and 131°, the solution evaporated to dryness by a water bath, the residue lixiviated with alcohol of 0.843 density, and the filtered solution distilled to a syrup, from which after the addition of a little water the hematoxylin is gradually deposited.

It crystallizes in reddish yellow scales, soluble in 1000 times their weight of water, dissolving easily in alcohol and ether. Acids in small quantity make it yellow, in large quantity red. The alkaline bases impart to a solution of hematoxylin a violet, purple or blue colour. Its decoction is deprived of colour by sulphuretted hydrogen (which has the same action on litmus,) and by nascent hydrogen; much of the hematoxylin probably exists in this state in the wood and acquires colour in the course of its application as a dye. Cloth impregnated with alumina is dyed *black* in a decoction of logwood, and of a fine brown in a mixture of logwood and madder. It enters into the materials for dyeing hats and broad cloth black; the effect of an acid in staining them red is due to its presence. By dry distillation hematoxylin yields ammonia, proving that it contains nitrogen.

BREZILIN.

This name has been applied by Chevreul to the colouring matter of Brazil wood, which comes to this country from Brazil and Pernambuco, and is the wood of several species of *Cæsalpina*. It is obtained by similar processes with the preceding colouring matters.

Brezilin crystallizes in orange prisms, soluble in water and alcohol. Acids give it a yellow colour; with citric acid the yellow is particularly fine. When neutralised with alkali it becomes again of a fine red, but with an excess of alkali violet or blue. In the tree it is nearly colourless, owing to the presence of free acid, and its fine red colour does not appear till all the acid which it naturally contains is saturated. This saturation is generally effected by sprinkling the ground wood with a solution of carbonate of soda, when its colour is said to be raised. A very minute quantity of alkali gives an infusion of Brazil wood a violet colour, so that it is a delicate test of alkalinity. Alum and the acetate of alumina throw down from it an abundant carmine precipitate, while the liquid retains the same colour; these compounds form the basis of common red ink. For some years past brazil-wood has been nearly superseded in this country by a wood imported from Africa, and named *camwood* by dyers, which is richer and gives a finer colour than any of the varieties of Brazil wood. It is also not so much affected by alkalies, nor so liable to assume a violet shade; and the yellow colouring matter with which it is mixed gives the red a more lively appearance (Dr. Thomson.) But the colour of these and all other red woods has little permanence and does not produce fast colours.

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* Ann. de Chim. et de Phys., t. 81, p. 128.

BERBERIN.

This is a crystalline substance of a fine yellow colour derived by the MM. Buchner from the bark of barbery root, *Berberis vulgaris*.* The root is exhausted by means of boiling water, the decoction concentrated to the consistence of a soft extract, and this digested repeatedly in alcohol of 0.844, so long as the liquid acquires a bitter taste. These tinctures are filtered, a considerable portion of alcohol distilled off, and the residue left in an open vessel to crystallize in a cool place. It forms fine prisms of a clear yellow colour, without odour, but having an intensely bitter taste. It is not fusible without decomposition. It is sparingly soluble in cold water, largely soluble in hot water, soluble in alcohol, forms compounds with bases, and precipitates readily all metallic salts. Its composition is expressed by $C_{33}H_{18}NO_{12}$. Berberin answers very well as a dye stuff, and gives a fixed yellow on cotton cloth without any mordant. It forms also a powerful tonic.

QUERCITRIN.

The yellow colouring matter of quercitron bark has lately been examined by M. Bolley.† It was obtained from a decoction of the bark clarified by albumen, and having its tannin precipitated by isinglass, evaporated to an extract and treated as usual with strong alcohol. It requires about 400 parts of boiling water for solution, but dissolves in 4 or 5 parts of absolute alcohol. It is deposited in little cauliflower looking masses, which by a magnifying power of 10 times are seen to be composed of small crystals. It yields by dry distillation a yellow liquid; which soon solidifies as a clear yellow mass; this Chevreul considered as unaltered quercitrin. As it restores the colour of reddened litmus paper, and combines with and neutralises bases, M. Bolley considers it an acid and names it *Quercitronic acid.* The formula of the crystallized acid, which agrees with analysis, is $HO+C_{16}H_8O_9$, of the salt of lead $PbO+C_{16}H_8O_9$. Herm. Trommsdorff found *polychrome* to have the same composition, and represented it by the same formula halved.*

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* Journal de Pharmacie, t. 17, p. 40 and t. 21, pp. 309, 408.

† Liebig's Annalen, xxxvii, 101.

CHAPTER VIII.

ACIDS.

SECTION I.

ACIDS SUPPOSED TO CONTAIN CARBONIC OXIDE.

Carbonic acid, and chlorocarbonic acid, may be considered as combinations of carbonic oxide, as they are formed by the union of that radical with oxygen and chlorine. Carbonic oxide also unites with potassium, and by the decomposition of this compound, croconic and rhodizonic acids are produced. Oxalic and mellitic acids also appear from their composition to contain the same radical.

OXALIC ACID.

Formula of the hydrated acid, HO,C_2O_3+2HO. This acid, discovered by Scheele in 1776, exists in the form of an acid salt of potash, in a great number of plants, particularly in the species of Oxalis and Rumex; combined with lime it also forms a part of several lichens. Oxalate of lime occurs likewise as a mineral, humboldtite, and forms the basis of a species of urinary calculus. This acid is also produced by the oxidation of carbon in combination, in a variety of circumstances, being the general product of the oxidation of organic substances by nitric acid, hypermanganate of potash, and by fused potash. Those matters which contain oxygen and hydrogen in the proportion of water, furnish the largest quantity of oxalic acid.

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* Liebig's Annalen, xiv, 205.

This acid has been derived in quantity from lichens, but it is usually prepared by acting upon 1 part of sugar, or better, starch, by 5 parts of nitric acid, of 1.42, diluted with ten parts of water at a gentle heat till no gas is evolved, and evaporating to crystallise. The crystals must be drained, and crystallized a second time, as they are apt to retain a portion of nitric acid.

It forms long, four-sided, oblique prisms, with dihedral summits, or terminated by a single face. These crystals contain three atoms of water, one of which is basic, and the other two constitutional, or water of crystallization. The latter two may be expelled at a temperature above 212°, and the protohydrate rises at the same time in vapour, and condenses as a woolly sublimate. Heated in a retort, the hydrated acid undergoes decomposition about 311°, and is converted into carbonic oxide, carbonic acid, and formic acid, without leaving any fixed residue. Nitric acid, with heat, converts oxalic acid into water and carbonic acid. When heated with sulphuric acid, oxalic acid yields equal volumes of carbonic oxide and carbonic acid; C_2O_3 being equivalent to $CO + CO_2$, (page 308). No charring, nor evolution of any other gas occurs, so that the action of concentrated sulphuric acid affords the means of recognising oxalic acid or any oxalate. Crystallized oxalic acid is soluble in 8 parts of water, at 59°, in its own weight of boiling water, and in 4 parts of alcohol, at 59°.

Oxalates.—With potash, and with ammonia, oxalic acid forms neutral oxalates, binoxalates, and quadroxalates. Oxalate of *potash*, $KO,C_2O_3 + HO$, contains 1 atom of water of crystallization, which it loses a little above 212°; it crystallizes generally in prisms of six unequal sides, terminated by oblique dihedral summits; these crystals are soluble in 3 parts of water, insoluble in alcohol. *Binoxolate of potash*, KO,C_2O_3+HO,C_2O_3+2HO, is sold under the name of salt of sorrel; it crystallizes in oblique, diaphanous rhomboidal prisms, which are soluble in 40 parts of cold water, 6 parts of hot water, and insoluble in alcohol. *Quadroxalate of potash*, $KO,C_2O_3+HO,C_2O_3+2(HO,C_2O_3+2HO)$, crystallizes in oblique octohedrons, of which two angles are truncated. This salt appears to be a compound of 1 atom of binoxalate of potash, with 2 atoms of hydrated oxalic acid; the 4 atoms of water of crystallization, of the last mentioned constituent escape when the salt is heated to 262°, (page 172). Oxalate of *soda*, NaO,C_2O_3, is the only anhydrous alkaline oxalate, and is the least soluble of the salts of soda. There is also a binoxalate of soda. The oxalates of ammonia correspond in number and composition with the salts of potash. The neutral oxalate of *ammonia*, which is formed by neutralising oxalic acid with carbonate of ammonia, is much used as a reagent, particularly to separate lime from magnesia, and generally to precipitate lime. It is less soluble than oxalic acid. When distilled in a glass retort, by a heat gradually increased, oxalate of ammonia affords a dirty white sublimate of oxamide, $C_2O_2+NH_2$ (page 407), together with ammonia, carbonic acid, carbonic oxide, and cyanogen.

Oxalate of *lime*, CaO,C_2O_3+2HO is thrown down as a brilliant white precipitate, remarkable for its insolubility. It is insoluble in acetic acid, but soluble in nitric and hydrochloric acids. It leaves, when heated to incipient redness by a spirit lamp, a white residue of carbonate of lime, from which the proportion of oxalic acid, or of lime, may be inferred. The oxalates of *magnesia*, *zinc*, and *manganese*, have the same composition as the oxalate of lime. The first mentioned possesses a small degree of solubility, the others are insoluble. Oxalate of *copper* forms a double salt with oxalate of ammonia, which corresponds in composition with the binoxalate of ammonia. Oxalate of *barytes* is expressed by BaO,C_2O_3+HO; it is quite insoluble in water. Oxalate of *silver* is an insoluble white powder, which is anhydrous. (Phil. Trans. 1827, p. 47).

The double oxalates of *chronium*, and the aluminous class have already been described (pages 519, 566, and 611).

RHODIZONIC ACID.

Formula of the acid supposed anhydrous: C_7O_7. Of the salt of potash, $3KO+C_7O_7$; of the salt of lead $3PbO+C_7O_7$, (Thaulow).

This body, which derives its name from the red colour of its salts, was first observed by L. Gmelin, and recognised as a new acid by Heller. Potassium, gently heated in carbonic oxide, absorbs that gas with avidity, fusing of a green tint, and spreading over the sides of the vessel; afterwards the oxicarburet becomes black and porous. Allowed to cool, it is dissolved with water, when a violent disengagement of combustible gases occurs, and a red solution is formed, containing rhodizonate of potash. The same oxicarburet of potassium is formed in large quantity, as an accidental product in the preparation of potassium from carbonate of potash and charcoal, being found as a black mass in the neck of the retort, or in the receiver with the potassium. The salt from the oxicarburet may be deprived of the excess of caustic potash by alcohol, in which the rhodizonate of potash is insoluble.

Rhodizonic acid is apt to undergo decomposition in being liberated from its salts, and has not been obtained in a state of purity. All its salts are red, and in the dry state have a metallic lustre, and reflect green. Its potash salt undergoes a remarkable decomposition when its solution is heated, being converted into free potash, oxalate of potash, and croconate of potash:

$$3KO+C_7O_7=KO \text{ and } KO+C_2O_3 \text{ and } KO+C_5O_4.$$

CROCONIC ACID.

Formula of the acid supposed anhydrous, C_5O_4.

This acid derives its name from the saffron colour of its salts; it was discovered by L. Gmelin. The croconate of potash is deposited in long yellow and brilliant needles from a solution of rhodizonate of potash, which has been decomposed by ebullition. The acid may be obtained free, by decomposing croconate of potash by hydrofluosilicic acid, and evaporating to dryness. It is strongly acid, crystallizes of a yellow colour easily, and is soluble in alcohol.

Croconate of potash, KO,C_5O_4+2HO, crystallizes in long orange prisms of 6 or 8 sides, having a nitrous taste; loses its 2 atoms of water at a moderate heat and becomes lemon yellow. It is insoluble in alcohol, in common with all the salts of this acid, except the croconate of ammonia which is soluble in alcohol.

Croconate of lead, PbO,C_5O_4+HO, precipitates in golden yellow micaceous plates, when a hot and dilute solution of acetate of lead is added to a solution of croconate of potash containing acetic acid.

Hydrated croconic acid has been considered as a hydracid, $H+C_5O_5$, that is, a compound of hydrogen, and a salt-radical; a constitution which is analogous, being assigned to mellitic acid.

The gas evolved when oxicarburet of potassium is dissolved in water is not pure hydrogen, but contains carbon, and is distinguished, according to Mr. E. Davy, from all the other carburets of hydrogen, by the property it possesses of inflaming at the ordinary temperature and depositing carbon, when mixed with an equal volume of chlorine.

MELLITIC ACID.

Formula of the crystallized acid: H,C_4O_4, or $HO+C_4O_3$ of the mellitates dried at 212°, M,C_4O_4+HO, or MO,C_4O_3+HO.

This acid was discovered by Klaproth in a rare mineral, *mellite*, which is the mellitate of alumina. The free acid is best obtained, according to Wœhler, by decomposing the mellitate of lead by sulphuretted hydrogen; it is a white crystalline powder, soluble in water and alcohol; from the last of which it crystallizes by slow evaporation in needles radiating from a centre. The dry acid is not altered by a temperature of 572° (300° centig.), nor is it decomposed by boiling nitric or sulphuric acid.

Mellitates.—Potash, soda and ammonia form acid besides neutral mellitates. Nitrate of potash forms a remarkable double salt with bimellitate of potash, $KO,NO_5+4(HO,\bar{M}+KO,\bar{M})+6HO$, described by Wœhler. It is remarkable that the nitrates particularly give rise to combinations in such proportions. Neutral mellitate of *ammonia* undergoes a remarkable decomposition by heat, which has been lately investigated by Wœhler. Heated for some time between 302° and 320°, it loses ammonia, and is transformed into a pale yellow powder, which water decomposes into two substances, one of which, *paramide*, is white and insoluble, and the other a soluble ammoniacal salt, of which the acid is named *euchronic* (from ευχροος, of a fine colour). The composition of paramide is C_8HNO_4; it appears to be formed from 2 atoms of mellitate of ammonia, $C_8H_8N_2O_8$, by the loss of 1 atom of ammonia and 4 atoms of water. By boiling with water, particularly under pressure at 392° (200° centig.), it is converted into acid mellitate of ammonia.

Euchronic acid, $2HO,C_{12}NO_6+2HO$, is separated from the above acid ammoniacal salt by nitric or hydrochloric acid. It crystallizes in very small, colourless, rhomboidal prisms, which have a strong acid taste, and dissolve with difficulty; they lose 2HO at 392°. It fuses and is decomposed above 536°. When crystallized euchronic acid is heated to 392°, in a glass tube hermetically sealed, with a quantity of water insufficient to dissolve it, a complete solution is obtained, in which, however, the euchronic acid is converted into acid mellitate of ammonia. Euchronic acid is distinguished from all other organic compounds by the way in which it comports itself with metallic zinc. A slip of zinc dipt in a solution of this acid, immediately becomes of a magnificent blue colour at its surface; this colour becomes at the boiling point nearly as intense as that of indigo. Washed and dried, it forms a black mass which contains no zinc. When slightly heated, even upon paper, it becomes immediately completely white, and is changed anew into euchronic acid. M. Wœhler applies the name *euchrone* to the blue compound, and considers that the action of zinc in its formation is a deoxidating one, euchrone being an inferior degree of oxidation of the radical of euchronic acid, or that radical itself; but from want of material this singular and most interesting body was not fully investigated. (Ann. de Chim. &c. 3 sér. ii, 78).

Mellitate of silver undergoes a particular decomposition at 356°, losing an atom of water, and becoming Ag,C_4O_4.

Mellitate of alumina, native mellite or honeystone is composed of $Al_2O_3,3C_4O_4H+18HO$, according to Wœhler. It crystallizes in regular octohedrons, of a honey-yellow colour; is insoluble in cold water, and decomposed by boiling water.

SECTION II.

MECONIC ACID AND ITS CONGENERS.

Meconic acid, $3HO,C_{14}HO_{11}+6HO$, is a tribasic acid, which crystallizes with 6 atoms of water of crystallization. It is found only in opium, of which it is the characteristic acid; it is named from μηκων, the poppy. It is best obtained by decomposing meconate of potash dissolved in 16 to 20 parts of hot water with 2 or 3 parts of pure hydrochloric acid, and crystallizes on cooling. The solutions in this process must neither be boiled, nor filtered through paper, as the latter may contain iron. (Robiquet). It crystallizes in pearly plates, which are soft to the touch, and possess an acid and astringent taste. It is sparingly soluble in cold water, but very soluble in hot water; it is equally soluble in alcohol. Salts of the peroxide of iron produce a deep red solution with meconic acid, without occasioning any precipitate. Chloride of mercury does not destroy the colour of this solution (Parnell), a property by which meconic acid may be distinguished from the persulphocyanide of iron, which is also red, but becomes yellow when chloride of mercury or gold is added to it.

A concentrated solution of meconic acid becomes yellow, when boiled, and then deep brown, and there are formed carbonic acid, oxalic acid, comenic acid, and a dark brown matter. Boiling dilute sulphuric acid, or hydrochloric acid, converts it with effervescence into carbonic acid and comenic acid.

The *meconates* contain all 3 atoms of base, one of which is generally water. Meconate of *lead* contains 2 atoms of oxide of lead; it is an insoluble white powder, which is thrown down from a solution of opium by acetate or subacetate of lead. After being washed, it is diffused through water and decomposed by a stream of sulphuretted hydrogen, to liberate the meconic acid, which may then be indicated by a persalt of iron; becoming of a wine-red colour.

Comenic acid, $2HO,C_{12}H_2O_8$, a bibasic acid, which crystallizes in very hard crusts or crystalline grains, with nothing more than its basic water. It is formed, as already stated, on boiling a solution of meconic acid with a pretty strong acid; also by heating dry meconic acid to 392°, when carbonic acid is disengaged till the temperature rises to 446°, when the meconic acid is found to be entirely converted into comenic acid. In this transformation, the former hydrated acid loses 2 atoms of water and 2 atoms of carbonic acid: $C_{14}H_4O_{14}=C_{12}H_2O_8$ and H_2O_2 and C_2O_4.

Comenic acid dissolves in 16 parts of boiling water; its solution decomposes the alkaline carbonates, and reddens salts of peroxide of iron. At 572°, it is decomposed and resolved into water, carbonic acid and pyromeconic acid. The comenates contain all two atoms of base, one of which is occasionally water.

Pyromeconic acid, $HO,C_{10}H_3O_5$, a monobasic acid, which presents itself as a colourless sublimate, composed of brilliant flattened plates, when crystallized comenic acid is submitted to dry distillation: $C_{12}H_4O_{10}=C_{10}H_3O_5$ and HO and C_2O_4. Its taste is styptic, with a bitter after-taste; it fuses between 248° and 257° into an oily liquid, and sublimes without leaving any residue. It is very soluble both in water and alcohol. It reduces a solution of gold, and communicates a red colour to solutions of peroxide of iron. Its salt of *lead* is a white precipitate, of the composition, $PbO,C_{10}H_3O_5$.

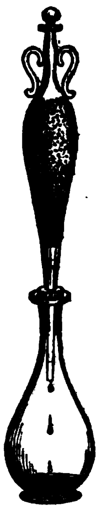
SECTION III.

TANNIC ACID AND BODIES ALLIED TO IT.

The formula of tannic acid or *tannin* dried at 212° is $3HO+C_{18}H_5O_9$: it is a tribasic acid.

Tannic acid occurs in the bark of all the varieties of Quercus and many other trees, and in gall-nuts, from which it is procured in greatest purity. It is prepared, after Pelouze, in a percolator or apparatus of displacement, fig. 95, the lower opening of which is closed by a plug of cotton, and the vessel entirely filled with broken gall-nuts, which are more suitable for the experiment than the powder of gall-nuts. Over the gall-nuts as much aqueous ether is poured as the vessel will contain, and the mixture left to digest for several hours. The liquid is then permitted to run off into the caraffe below, by loosening the stopper above and admitting air. It is found to divide into two liquids, of which the denser syrupy and yellowish one, is a very concentrated solution of tannic acid in water, and the lighter, which is coloured green, an ethereal solution of gallic acid and other matters. Additions of ether are made to the gall-nuts, so long as two different liquids flow from the lower orifice. The aqueous ether employed is obtained by agitating common ether with water. If the gall-nuts be moistened with water before the addition of the ether, the solution of tannin which comes off is highly coloured; but if the gall-nuts be merely exposed to steam, and washed in the percolator with anhydrous ether, the process succeeds equally well as with the aqueous ether.

FIG. 95.



By the evaporation of the solution of tannin, a yellow light mass is generally obtained, which is purified by solution in water, and evaporation in vacuo over sulphuric acid. It then forms a mass colourless or slightly yellow, which is not crystalline but resembles dried gum, and becomes somewhat deeper in tint in humid air, but is not otherwise altered. It is dissolved easily by water and in large quantity; the taste of the solution is purely astringent without bitterness, it reddens vegetable blues, and decomposes alkaline carbonates with effervescence. Tannic acid is soluble in aqueous alcohol, but only very slightly soluble in ether. Its solution is affected by air, particularly at a high temperature, oxygen being absorbed and an equal volume of carbonic acid evolved, while the tannic acid is transformed into gallic and ellagic acids. But the solution of tannic acid keeps without change in close vessels. A moderately strong solution of tannic acid gives with sulphuric, hydrochloric, phosphoric, arsenic or boracic acid, a thick white precipitate, which is a compound of the two acids mixed, and is very soluble in pure water and in alcohol. When the solution of tannic acid is precipitated hot by sulphuric acid, a resinous mass is formed, which dissolves in dilute sulphuric acid at the point of ebullition, of a deep tint, and after being boiled for some minutes is converted, without any evolution, of gas, into gallic acid, which crystallizes on the cooling of the solution.

Tannic acid boiled in an excess of caustic alkali, undergoes the same transformation.

Tannic acid precipitates animal gelatine entirely from solution in thick flocks, which adhere and form a viscid elastic mass when the acid is in excess; this precipitate dissolves in the supernatant liquid at the boiling point. It is known as *tanno-gelatin*, and contains about half its weight of tannin. Tannin is also absorbed from solution by the fresh skin of animals, which is then tanned or converted into leather, and ceases to be soluble in water or to be putrescible. Tannic acid also precipitates a solution of starch and of albumen, and is capable of combining with animal fibrin.

Tannates.—The neutral tannate of potash or ammonia appears as a thick precipitate, when a moderately dilute solution of tannic acid is treated with that alkali or its carbonate; the precipitate is very soluble in an excess of alkali. Tannates of barytes, strontian, lime, and magnesia are very sparingly soluble. Salts of protoxide of iron undergo no alteration when mixed with a solution of tannic acid, but if exposed to air become soon of a deep bluish black colour. Tannate of *peroxide of iron* is a black pulverulent precipitate, $Fe_2O_3,C_{18}H_5O_9+9HO$ (Pelouze), formed on adding persulphate of iron to a solution of tannic acid; it is the basis of writing ink. A good black ink is prepared from bruised Aleppo galls 6 ounces, copperas (sulphate of iron) 4 ounces, gum arabic 4 ounces, water 6 pints. The galls are boiled in the water, the other ingredients then added, and the whole kept in a wooden or glass vessel and occasionally shaken. In two months strain, and pour off the ink into glass bottles to be well corked. To prevent mould, add one grain of corrosive sublimate or three drops of creosote to each pint of ink. (Brande's Manual, p. 1105). Tartar emetic gives a white precipitate with tannic acid, the tannate of *antimony*, $HO_3+3C_{18}H_5O_9$. Tannic acid forms sparingly soluble white precipitates with most of the organic bases.

GALLIC ACID.

Formula of the crystallized acid, $2HO,C_7HO_3+HO$; of the acid dried at 212°; $2HO,C_7HO_3$. Of one gallate of lead dried at 212°: $HO,PbO.2C_7HO_3+HO$; the last atom of water is lost at 320°. Of another gallate of lead: $2PbO,C_7HO_3$. Of acid gallate of ammonia, the composition is expressed by $NH_4O,C_7HO_3+2HO,C_7HO_3$; it loses nothing at 212°. These are the only salts of gallic acid of which the composition is certainly known, and they are not sufficient to determine whether or not gallic acid is bibasic.

The metamorphosis of tannic acid into gallic acid, under the influence of boiling dilute sulphuric acid has already been adverted to. The same change occurs in an aqueous extract of gallnuts exposed to air for several months. By the absorption of 8 atoms of oxygen, 1 atom of hydrated tannic acid might be converted into 2 atoms of hydrated gallic acid, 4 atoms of carbonic acid, and 2 atoms of water: $C_{18}H_8O_{12}$ and $O_8=2C_7H_3O_5$ and $4CO_2$ and 2 HO. Much ellagic acid is also formed in the transformation of the tannin of gallnuts, in the air. To prepare gallic acid, a strong extract of gallnuts in cold water may be precipitated in the cold by sulphuric acid; the thick mass be mixed with dilute sulphuric acid, expressed while still humid, and introduced in this state into a mixture of sulphuric acid with two parts of water at the boiling temperature. The liquid is boiled for some minutes and then allowed to cool; crystals of gallic acid are deposited, which may be purified by crystallizing again from water, converting the new product, which is still coloured, by means of acetate of lead into an insoluble gallate of lead, which last is washed, then diffused through water, and decomposed by a stream of sulphuretted hydrogen gas; the sulphuret of lead, which is then formed, assists in carrying down the colouring matter.

Gallic acid crystallizes on cooling from a hot solution, in thin, silky needles. It requires 100 parts of cold water to dissolve it, but is soluble in 3 parts of boiling water. It is also very soluble in alcohol, and to a small extent in ether. When pure it does not precipitate a solution of gelatine. The aqueous solution of this acid may be kept apart from air without change, but with access of oxygen it undergoes decomposition, a brown matter being deposited, while carbonic acid is evolved and the surface becomes covered with mouldiness. This decomposition is greatly promoted by the presence of a mineral acid, or of an alkali in the solution. With salts of peroxide of iron gallic acid assumes a deep blue tint; the black precipitate which falls, left in contact with gallic acid, is gradually reduced to the state of protoxide, but not when a salt of the ferrosoferric oxide has been employed in its formation.

When crystallized gallic acid is dissolved in concentrated sulphuric acid, and the solution heated, it assumes a crimson tint at a temperature above 284°. If allowed to cool in this state, and cold water afterwards added, an abundant precipitate is formed of a reddish brown colour and crystalline aspect, which appears to be gallic acid that has lost an atom of water, its composition after drying being $C_7H_2O_4$ (Robiquet). It is insoluble in water, but dissolves easily in alkalies, and has some analogy, according to Robiquet, to the colouring matter of madder. It is decomposed by dry distillation, giving small cinnabar-red prismatic crystals.

All the *gallates* are remarkable for the facility with which they absorb oxygen, when in contact with an excess of alkali; carbonic acid is then formed and a brown matter insoluble in water. In a mineral water alkaline from the presence of lime or magnesia, an addition of gallic acid causes the liquid gradually to become turbid from the formation of a black precipitate, although no iron be present, owing to the decomposition of the gallic acid itself.

Pyrogallic acid, $C_6H_3O_3$, or $C_8H_4O_4$ (the equivalent being doubtful), is prepared by heating briskly either tannic or gallic acid, previously well dried, in a retort by means of a spirit-lamp till coloured empyreumatic products come over. The pyrogallic acid is obtained as a crystalline sublimate, which may be purified by a second sublimation at a gentle heat. It forms white plates or needles, fuses at 239°, boils at 410°, and sublimes without alteration. It does not redden litmus; its taste is bitter and slightly astringent. It dissolves in 2¼ parts of water at 55°.4 (13° centig.); the solution absorbs oxygen and deposits a brown powder. It is equally soluble in alcohol and ether. When heated briskly above 482° (250° centig.), pyrogallic acid blackens, and is converted into water and metagallic acid.

Pyrogallate of lead, a white precipitate formed on adding a solution of pyrogallic acid to acetate of lead, is $PbO,C_6H_6O_3$, according to Berzelius, and also Pelouze, but $PbO,C_8H_8O_4$ according to the later analysis of R. C. Campbell.

Metagallic acid, melangallic acid (Berzelius). The formula of the anhydrous acid is $C_6H_2O_2$ (Pelouze); its probable atomic weight: $HO,C_{12}H_3O_3$. This body remains as a fixed residue in the retort when gallic acid or tannic acid is heated by an oil bath to 482°, till all the volatile products escape. It is then dissolved in a solution of alkali and precipitated by an acid to obtain it in a state of purity. It is a black powder, insoluble in water, which forms soluble compounds with alkalies of a deep black colour.

Tannic and gallic acids, although differing so much in composition, afford the same products when decomposed by heat. This is explained by supposing tannic acid a compound of gallic and pyrogallic acids. In fact 3 atoms of tannic acid contain the elements of 6 atoms of gallic acid, and 2 atoms of pyrogallic acid.

$$3\ (C_{18}H_8O_{12})=6\ (C_7H_3O_5)+2\ (C_6H_3O_3).$$

Ellagic acid.—The gallic acid which forms in an infusion of gallnuts exposed to air, is always accompanied by a grey powder, which being insoluble, may be purified by boiling water; it is the acid in question. Ellagic acid dissolves in alkalies and is precipitated by acids. According to Pelouze it possesses the same composition as dried gallic acid, $C_7H_3O_5$; between 212° and 248°, it loses an atom of water and becomes $C_7H_2O_4$.

Catechu, the brown dried extract of the *Acacia* or *Mimosa catechu* contains a large quantity of tannic acid differing little from the tannic acid of gallnuts, which may be extracted by cold water. The portion insoluble in cold water, contains a particular principle *catechin*, $C_{15}H_6O_6$ (Swanberg). Two acids are produced when catechin with alkalies or alkaline carbonates absorbs oxygen from the air, and forms black solutions with the former and red with the latter; which have been named *japonic acid*, $HO+C_{12}H_4O_4$, and *rubinic acid*, $HO,C_{18}H_6O_9$ (Swanberg.)

SECTION IV.

CITRIC ACID AND THE PRODUCTS OF ITS DECOMPOSITION.

Formula of citrate of silver, $3AgO+C_{12}H_5O_{11}$. Of the crystals of citric acid formed on the cooling of a solution saturated at 212°, $3HO,C_{12}H_5O_{11}+HO$, which may be named hydrate A; this hydrate loses no weight and preserves its transparency at 212°. It is the type upon which most of the citrates are formed. Of the crystals formed by the spontaneous evaporation of a solution saturated in the cold, the formula is $3HO,C_{12}H_5O_{11}+2HO$; of which the two atoms of water of crystallization are lost at 212°.

Citric acid was discovered by Scheele; it exists in a considerable variety of plants, but is procured only in quantity from the orange and lemon and from gooseberries. The acid juice of these fruits is neutralised by a known weight of carbonate of lime; the insoluble citrate of lime washed, and then decomposed by a quantity of oil of vitriol equal in weight to the carbonate of lime used, diluted with 5 parts of water. The acid liquid is separated by filtration from the insoluble sulphate of lime; and the citric acid crystallized with a slight excess of sulphuric acid present, which is observed to favour the crystallization, while it is impeded by citrate of lime in solution.

Citric acid crystallizes in regular rhomboidal prisms, terminated by four faces, has an agreeable acid taste, and is soluble in an equal weight of water forming a thick syrup. A dilute solution of citric acid in water does not keep, but becomes covered with mouldiness. When pure, citric acid dissolves completely in alcohol, without residue, and does not give a precipitate with lime-water. But when a few drops of the acid are added to the latter in excess, the clear liquid obtained becomes turbid when heated, from the deposition of a white basic citrate of lime, $3CaO,C_{12}H_5O_{11}+CaO,HO$, which dissolves in acids without effervescence. Citric acid is commonly distinguished by that property. Hydrate A of citric acid, which contains 4 atoms of water fuses at 266°, and loses nothing, although hydrate B, which contains 5HO, loses 2HO at 212°. When the temperature of 302° is exceeded the acid of both hydrates undergoes decomposition. When 1 part of crystallized citric acid is gently heated with 4 parts of oil of vitriol, a considerable quantity of carbonic oxide is evolved, and acetic acid is formed. When fused with an excess of hydrate of potash, citric acid is decomposed into oxalic and acetic acids; 1 atom of citric acid containing the elements of 2 atoms of acetic acid, 2 atoms of oxalic acid and 2 atoms of water.

Citrates.—The neutral salts of citric acid, besides 3 atoms of fixed base, carry along with them the atom of water of acid hydrate A; which water however they either abandon at the ordinary temperature, like the citrate of silver, or at a high temperature. In certain subcitrates this atom of water is replaced by an atom of metallic oxide, such as lime or oxide of lead. The composition of these salts has received considerable attention. The following are the formulæ of the most remarkable citrates:

Citrates of *potash:* three salts exist containing as base respectively, $3KO$; $2KO+HO$; and $KO+2HO$. Citrates of *soda:* salt *A*, $3NaO,C_{12}H_5O_{11}+11HO$ (Berzelius); loses $7HO$ at 212°, and the remaining $4HO$ between 374° and 392° (190° and 200° centig.). Salt *B*, $2NaO.HO,C_{12}H_5O_{11}$. Salt *C*, $NaO.2HO,C_{12}H_5O_{11}$. Citrate of *barytes*, $3BaO,C_{12}H_5O_{11}+7HO$ (Berzelius); loses $6HO$ at 302° and becomes anhydrous at 374°. Another citrate of barytes appears to be a compound of the preceding salt, with $2BaO.HO.C_{12}H_5O_{11}$, its empyrical formula being $2C_{12}H_5O_{11}+5BaO+8HO$. Citrate of *lime*, $3CaO,C_{12}H_5O_{11}+4HO$ (Berzelius); it loses $3HO$ at 212°, and the remaining HO at a higher temperature. The subcitrate of lime lately mentioned loses HO at 212°. Citrates of *lead:* salt *A*, $3PbO,C_{12}H_5O_{11}+HO$. Salt *B*, $2PbO.HO,C_{12}H_5O_{11}+2HO$. Salt *C*, $3PbO,C_{12}H_5O_{11}+3PbO$. Salt *D*, $3PbO,C_{12}H_5O_{11}+PbO,HO$. Citrate of *copper*, $3CaO,C_{12}H_5O_{11}+CaO$. Citrate of *silver*, $3AgO,C_{12}H_5O_{11}+HO$; loses HO between 68° and 77°. Citrate of *antimony* and *potash*, $SbO_3,C_{12}H_5O_{11}+3KO,C_{12}H_5O_{11}+5HO$ (Thaulow); it crystallizes in prisms of a brilliant whiteness which lose their whole water of crystallization at 212°. Citrate of *ethyl* $3EO,C_{12}H_5O_{11}$. (Liebig's Traité, ii, 45.)

Aconitic acid, $HO+C_4H_2O_3$.—When crystallized citric acid is heated, it fuses, gives off water, but undergoes no essential change till inflammable gases are disengaged, and afterwards an acid liquid which condenses in oily striæ, with carbonic acid gas. These appearances indicate two stages in the distillation, and if the process be interrupted when the disengagement of water and inflammable vapour ceases, the fixed residue in the retort contains no citric acid, but a new acid produced by its decomposition, which proves to be the same with the acid from the *Aconitum napellus* and *Equisetum fluviatile*, and which was already known under the names of aconitic and equisetic acid. This acid is soluble in ether, which citric acid is not. It is also readily converted into aconitic ether, by the action of dry hydrochloric acid upon its solution in alcohol, and is precipitated by water, while citric acid not being etherified by this process remains in the liquor. Aconitic ether is easily decomposed by caustic potash, and the acid may be derived from the potash salt. Aconitic acid forms only small confused crystals. When briskly distilled it affords the two following isomeric acids, which sublime (see page 712.)

Itaconic acid, $HO+C_5H_2O_3$; known also as pyrocitric acid and citricic acid. It crystallizes in rhomboidal tables, is soluble in 17 parts of water at 50°, in 10 at 68°; soluble also in alcohol and ether.

Citraconic acid (hydrated), $HO+C_5H_2O_3$; distinguished also as citribic acid by M. Baup. It is obtained anhydrous by distillation as an oily limpid liquid, $C_5H_2O_3$, which distils at 212° without decomposition.

SECTION V.

TARTARIC AND PARATARTARIC ACIDS AND THE PRODUCTS OF THEIR DECOMPOSITION.

TARTARIC ACID.

Formula of the crystallized acid, $2HO+C_8H_4O_{10}$; a bibasic acid.

This acid, which in common with so many others was first prepared by Scheele, exists in many fruits, and also as tartrate of lime in several roots, but is prepared only from the juice of the grape, which contains tartaric acid in the form of tartar or bitartrate of potash. The last salt precipitates during the fermentation of wine, owing to its insolubility in alcohol; in the crude state, it is known as *argol*, and is highly coloured, when purified, as cream of tartar. To procure tartaric acid, cream of tartar is dissolved in boiling water and neutralised with carbonate of lime, which throws down one half of the tartaric acid as an insoluble tartrate of lime; the other half of the acid contained in the neutral tartrate of potash, is precipitated by a solution of chloride of calcium. The tartrate of lime is decomposed by an equivalent quantity of sulphuric acid, and the tartaric acid separated from the insoluble sulphate of lime by filtration; 3 parts of oil of vitriol are usually taken for 5 parts of cream of tartar. The acid solution is evaporated in leaden vessels by a gentle heat, during which process some sulphate of lime is deposited. A syrupy solution of tartaric acid left in a warm place yields crystals which are oblique prisms of a rhombic base, terminated by dihedral summits and truncated on the longitudinal edges, or hexagonal prisms terminated by three faces of truncation; but the two parallel faces are generally more developed than the others, so as to give the crystals the appearance of tables. The crystals are persistent in air, of a strongly acid and agreeable taste, dissolve in 1½ parts of cold water and in less hot water, and are equally soluble in alcohol. The aqueous solution of tartaric acid and its salts undergoes decomposition, and becomes covered with mouldiness. When the crystallized acid is heated, it loses water and produces a series of new compounds. Treated at a high temperature with a strong solution of hydrate of potash, tartaric acid is entirely converted into acetate and oxalate of potash; one atom of crystallized tartaric acid actually containing the elements of 1 atom of hydrated acetic acid and two atoms of hydrated oxalic acid:

$$2HO + C_8H_4O_{10} = HO,C_4H_3O_3 \text{ and } 2\ (HO,C_2O_3).$$

A solution of tartaric acid does not disturb solutions of chloride of barium and chloride of calcium, but produces a white precipitate in barytes and lime-water, and in acetate of lead. A solution of tartaric acid is also used in precipitating potash from its salts, when not very dilute, the bitartrate of potash falling down, upon agitation, as a granular precipitate, which is sparingly soluble in water, but dissolves readily in hydrochloric acid. The addition of tartaric acid to many metallic solutions, prevents their precipitation by alkalies.

Tartrates.—According as one or both atoms of water in tartaric acid are replaced by a metallic oxide, an acid or neutral tartrate is formed, and when the 2 atoms of metallic oxide are different, a double tartrate.

Neutral tartrate of *potash*, 2 $KO,C_8H_4O_{10}$ is anhydrous, and soluble in an equal weight of cold water. Acid tartrate of potash (bitartrate), $HO.KO,C_8H_4O_{10}$ is also anhydrous, soluble in 18 parts of boiling water, and in 184 parts of water at 68°; it is insoluble in alcohol. Purified tartar, when heated alone, gives a carbonaceous mixture (*black flux*), and when deflagrated with 2 parts of nitre, it leaves white carbonate of potash (*white flux*). Tuartrate of *potash* and *soda*, or rochelle salt, $KO.NaO,C_8H_4O_{10}+10HO$ (Schulze), is formed by neutralising acid tartrate of potash with carbonate of soda, is soluble in half its weight of cold water and persistent in air. It crystallizes with two equivalents of the tartrate of potash and boracic acid, and forms a double salt, which is anhydrous. Neutral tartrate of *ammonia*, $2NH_4O,C_8H_4O_{10}+2HO$ (Dulk). Acid tartrate of ammonia resembles acid tartrate of potash. A hot solution of this salt dissolves a large quantity of *arsenious acid*, and yields, by evaporation, large and transparent crystals of a salt of two bases, $NH_4O.AsO_3,C_8H_4O_{10}$, analogous in composition to tartrate of potash and antimony. Tartrate of *potash* and *boracic acid*, $KO.BO_3,C_8H_4O_{10}$ (Duflos), is a white uncrystalline mass, very soluble in water, obtained by dissolving a mixture of 47½ parts of cream of tartar (1 atom), and 15½ parts of crystallized boracic acid (1 atom), by means of hot water. Heated in a dry condition to 482° (250° centig.), this salt loses 2HO, like tartrate of antimony and potash, at the expense of the elements of the acid, the empyrical formula of the salt becoming $C_8H_2O_8,KO,BO_3$ (Soubeiran and Capitaine). Tartrate of *potash and peroxide of iron* is a pharmaceutical preparation; its composition when dried at 212° is $KO.Fe_2O_3,C_8H_4O_{10}$, (S. and C.). Tuartrate of *antimony* is a salt, crystallizing with difficulty, of which the composition is unknown. Three double tartrates of *antimony* and *potash* are known: (1) Tartar emetic (page 639,) the formula of which, dried at 212°, is $KO.SbO_3,C_8H_4O_{10}$, and heated to 392° (200° centig.), $KO.SbO_3C_8H_2O_8$. (2.) Tartar emetic combines with 3 atoms of the acid tartrate of potash, and forms a crystallizable double salt, when the mixture of these two salts is kept constantly boiling in the preparation of tartar emetic

(Knapp). (3). A salt $KO.SbO_3,2C_8H_4O_{10}+7HO$ (Knapp), formed by dissolving together 9 parts of tartar emetic, and 4 parts of crystallized tartaric acid, which is very soluble and crystallizable. Tartrate of *antimony* and *lead,* $PbO.SbO_3,C_8H_4O_{10}$ (Dumas), the white precipitate which falls on adding a salt of lead to a solution of tartar emetic, dried at 212°. Heated to 392°, it loses $2HO$, like tartar emetic.

Action of heat upon tartaric acid.—Tartaric acid fuses between 266° and 284°, and becomes brown at 320°. By the action of heat it loses first one fourth, then one half, and finally the whole of the water of its hydrate (Fremy), forming two new acids, the relation of which to tartaric will be best seen by doubling the formula of the latter:

Anhydrous tartaric acid . .	$C_{16}H_8O_{20}$
Tartrelic acid	$C_{16}H_8O_{20}+2HO$
Tartralic acid	$C_{16}H_8O_{20}3HO$
Crystallized tartaric acid . .	$C_{16}H_8O_{20}+4HO$

When the solutions of the modified acids are boiled, they are quickly converted into ordinary tartaric acid.* Representing anhydrous tartaric acid by $C_4H_2O_5$, we have then, for the modified acids, the following formulæ (Liebig):

$2(C_4H_2O_5)+2HO$ . .	crystallized tartaric acid.
$3(C_4H_2O_5)+2HO$ . .	tartralic acid.
$4(C_4H_2O_5)+2HO$ . .	tartrelic acid.

The salts of tartralic and tartrelic acids with alkaline bases are not crystallizable. Anhydrous tartaric acid is produced by keeping the crystallized tartaric acid for some time in an oil bath, at 302° (150° centig.); it is insoluble in cold water.

Tartaric acid yields the two following acids by its destructive distillation:

Liquid pyrotartaric acid, $HO,C_6H_3O_5$, which forms a monobasic ether and other salts.

Solid pyrotartraric acid, $HO,C_5H_3O_3$ (Pelouze), is formed only in small quantity by the distillation of tartaric acid, but in larger quantity by the distillation of acid tartrate of potash (Weniselos).

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* Fremy; Ann. de Chim. et de Phys. t. 68, p. 353.

PARATARTARIC (RACEMIC) ACID.

Liebig assigns to this acid, dried at 212°, the formula $HO + C_4H_2O_5$, which contains half the number of atoms in tartaric acid, and considers the former as a monobasic acid, while tartaric acid is bibasic. By this difference, the isomerism of these two acids (page 157) is accounted for. Crystallized paratartaric acid contains an additional atom of water, and is represented by $HO,C_4H_2O_5+HO$.

Paratartaric acid was discovered by Mr. Kestner, of Thann, and particularly studied by John, by Gay-Lussac and Berzelius. It forms no double salt of potash and soda, analogous to Rochelle salt, and is probably on that account monobasic. Paratataric acid is contained in the cream of tartar of the wines of the Vosges, and perhaps other localities, and is separated by neutralising that salt with carbonate of soda, and crystallizing out the tartrate of potash and soda. The mother liquor is precipitated by chloride of calcium, and the mixed tartrate and paratartrate of lime decomposed by sulphuric acid; on concentrating, the paratartaric acid crystallizes before the tartaric, being considerably less soluble.

Paratartaric acid crystallizes in oblique prisms, of a rhombic base, which effloresce in dry air. It is a more powerful acid than tartaric, decomposing nitrate and sulphate of lime and chloride of calcium, with precipitation of paratartrate of lime. Hence paratartaric acid was first mistaken for oxalic acid. The paratartrate of lime so formed, dissolves in hydrochloric acid, and is precipitated by ammonia.

Paratartrates.—These salts are identical in composition with the tartrates of the same base, but only a few of them have been examined. Paratartrate of *lead* is an insoluble white powder. Paratartrate of *antimony* and *potash* is prepared in the same way as tartar emetic, and has the same composition, but differs in crystalline form, being in four-sided prisms, of a rhombic base, or in needles grouped about a centre. Paratartaric acid has little disposition to form double salts.

According to the observations of Fremy, crystallized paratartaric acid loses water when heated, and gives rise to two new and peculiar acids, corresponding in composition with tartralic and tartrelic acids. At a still higher temperature, it gives rise to a body which is identical in properties with anhydrous tartaric acid. It gives also by dry distillation the same two pyrogen acids as tartaric acid.

SECTION VI.

MALIC ACID.

Formula of the hydrated acid; $2HO + C_8H_4O_8$. Malic acid is bibasic (Hagen).

This is the acid of apples, from which it derives its name, but is of frequent occurrence in other acidulous fruits and vegetable juices, where it is accompanied by citric and tartaric acids. It is generally prepared from the berries of the mountain ash (*Sorbus acuparia*). The fruit is collected in August, while scarcely red and before it is ripe. It is bruised in an iron mortar, the juice expressed, filtered through linen, and treated in a bason of copper with a thin milk of lime till the mixture commences to change colour. An excess of lime occasions a deep green coloration, but the liquid ought to have a slight acid reaction, and to retain a reddish brown colour. When now made to boil, a large quantity of a neutral malate of lime precipitates, crystalline and granular, which may be taken out as it collects, by means of a colander. After this is deposited, a new portion of milk of lime may be added, with the same precautions, and a fresh portion of malate of lime is obtained. This salt is washed cold, and introduced while still humid into a boiling mixture of 1 part of nitric acid and 10 parts of water, so as to dissolve it. A concentrated solution deposits on cooling a large crop of colourless and regular crystals, of the acid malate of lime. The addition of acetate of lead to the purified acid malate of lime, throws down a curdy white precipitate, which contains lime, but on allowing it to digest at a moderate heat in an excess of acetate of lead, the lime is abandoned, and crystals form in four-sided prismatic needles, grouped about a common centre, and possessing a silky lustre, which are neutral malate of lead, containing 6 atoms of water of crystallization.

The acid is now obtained by decomposing the malate of lead diffused through water, by a stream of sulphuretted hydrogen, the sulphuret of lead separated by filtration, and the liquid evaporated, first by the naked fire, and afterwards by a water-bath, to the consistence of a syrup. (Liebig).

The hydrated acid forms granular crusts, of which the crystallization is confused, and which are deliquescent. Its solution is very acid; it reduces the salts of gold; the dry acid dissolves entirely in alcohol. The crystallized acid fuses at 266° or 284° (130° or 140° centig.), but when kept for some time at that temperature, crystalline plates form in it, and gradually increase in quantity; these are *fumaric acid*, which is sparingly soluble in cold water. By dry distillation, malic acid affords water and afterwards a volatile and crystallizable acid, named maleic acid by Pelouze.

Malates.—Malic acid forms both neutral and acid salts with the alkaline and magnesian bases, the second atom of water in the acid salts being water. The malate of peroxide of iron is the only one which dissolves in alcohol.*

Maleic acid (hydrated), $2HO+C_8H_2O_3$. This acid comes over on the brisk distillation of malic acid. It crystallizes in plates or in oblique prisms of a rhombic base, is very soluble in water, alcohol and ether, its taste is acid and disagreeable. Distilled by a sharp heat it is decomposed, and resolved into water and a white volatile matter, *anhydrous maleic acid*, fusible at 134°.6, and boiling at 349°. There exist both a neutral and acid maleate of *silver*, the first containing 2 atoms of oxide of silver, and the last, 1 atom of oxide of silver with 1 atom of water as base, so that maleic acid is certainly bibasic.

Fumaric acid, $HO+C_4HO_3$; a monobasic acid, produced by heating malic acid, and also existing in fumitory (*Fumaria officinalis*), and in Iceland moss. The same acid is formed when the malates of an alkaline base are exposed to a high temperature. Fumaric acid thus appears to be related to malic acid, as pyrophosphoric acid is to phosphoric acid; but Dr. Hagen did not succeed in transforming fumaric acid again into malic, by boiling a solution of the former. Fumaric acid crystallizes in fine micaceous plates, soluble in 200 parts of cold water; it is more soluble in hot water and also in alcohol. It crystallizes from boiling nitric acid without change. Fumaric acid may be sublimed from a spatula, in the open air, without leaving any residue, but is decomposed in a great measure when distilled in a retort. A volatile *fumaric ether* was formed by Hagen; and by digesting the latter with aqueous ammonia, *fumaramide*, $C_4HO_2+NH_2$, which is an amorphous powder, of brilliant whiteness, almost insoluble in cold water and in alcohol.

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* Dr. Hagen on Malic Acid; Memoirs of the Chemical Society of London, vol. i, p. 28.

SECTION VII.

KINIC OR QUINIC ACID.

The formula of neutral kinate of silver is $AgO+C_{14}H_{11}O_{11}$; of neutral kinate of lime, $CaO+C_{14}H_{11}O_{11}$, from which it is inferred that the formula of anhydrous kinic acid is $C_{14}H_{11}O_{11}$. The formula of the crystallized acid is $C_7H_6O_6$, or $C_{14}H_{12}O_{12}$ $=HO+C_{14}H_{11}O_{11}$. But the kinates of lead and copper appear to belong to another class, of which the acid is bibasic, and its hydrate $2HO+C_7H_4O_4$; the formula of the kinate of lead being $2PbO+C_7H_4O_4$, and the formula of the basic kinate of copper, $CuO.HO+C_7H_4O_4$ (Woskresensky).

Kinic acid was discovered, in 1790, by Hoffmann. It exists as kinate of lime in the bark of all the quinquinas, and according to Berzelius, accompanies gallic acid in the laburnum of many trees. In preparing quinine and cinchonine, by boiling the bark of quinquina with hydrochloric or sulphuric acid, and precipitating the alkali from the extract by an excess of lime, the kinate of lime remains dissolved, and is deposited from the solution evaporated to a syrupy consistence, in the state of crystals. The salt is decomposed by heating gently for several hours a mixture of 6½ parts of it, with 1 part of concentrated sulphuric acid diluted with 10 parts of water. The supernatant liquid is drawn off from the precipitated sulphate of lime, alcohol added to it so as to throw down the sulphate of lime remaining in solution; and finally, the clear solution is evaporated by a moderate heat to a syrupy consistence, and left to itself. The kinic acid crystallizes in voluminous crystals derived from a prism of rhombic base, greatly resembling tartaric acid; they are persistent in air. (Liebig's Traité, ii, 122).

Kinic acid is soluble in 2 parts of boiling water; it is also soluble in alcohol. By dry distillation it yields a volatile crystalline acid, of which little is known. Kinic and gallic acids appear to be related; indeed gallic acid, which is $C_7H_3O_5$, may be considered as a kinic acid $C_7H_4O_4$, in which 1 equivalent of hydrogen is replaced by 1 equivalent of oxygen (Liebig).

Kinates.—All the kinates are soluble in water, with the exception of the kinate of lead containing 2 atoms of oxide of lead; alcohol precipitates them from their aqueous solutions.

Kinoïle is a product of the calcination of a kinate by a gentle heat, and of the action of peroxide of manganese and sulphuric acid upon crystallized kinic acid. It is a remarkable neutral substance, of a golden yellow colour and high lustre, heavier than water, fusing and volatilising without decomposition at 212° (Woskresensky).

SECTION VIII.

VOLATILE ACIDS OF BUTTER.

Butyric acid, $HO,C_8H_{5\frac{1}{2}}O_3$ (Chevreul). This is an oily limpid liquid, having the odour of rancid butter and a nauseous and ethereal taste. Its density is 0.9765 at 77°; it evaporates easily in the open air, and boils above 212°. By distillation butyric acid gives *butyrone*, C_6H_6O (Kraues), the formula of butyric acid being supposed $C_7H_6O_3$ (Loewig).

Caproic acid, $HO+C_{12}H_9O_3$ (Chevreul), is an oily limpid liquid, having the odour of sweat and a nauseous taste, with a sweetish after-taste of apples. Its density is 0.922 at 71.°8, it evaporates in open air, boils above 212°, is soluble in 96 parts of water at 44°.6. It is miscible with alcohol, ether and oils.

Capric acid, $HO+C_{18}H_{14}O_3$ (Chevreul), when liquid, greatly resembles caproic acid in physical properties. When agitated at 52°.7 it forms a mass of fine needles, which become entirely liquid at 64°.4. It has the same odour as caproic acid, with that also of the goat. It is dissolved by alcohol in all proportions, and is soluble in 6 parts of water at 68°.

When butter is melted with water, buttermilk, cheese and other impurities are separated from it, and the pure oil rises to the surface. It consists of margarine, oleine, butyrine, caprone, and caprine. The three latter are in small quantity, but it is to them, that the peculiar pleasant smell and taste of fresh butter are owing. They are compounds of oxide of glyceryl (page 877) with butyric, caproic and capric acids.

Hircic acid, was discovered by Chevreul in the fat of the goat; its composition is unknown.

Phocenic or *delphinic acid*, $HO + C_{10}H_7O_3$ (Chevreul); another volatile acid contained in train oil or seal oil, and in the berries of *Viburnum opulus*. Phocenic acid is a colourless liquid which burns like a volatile oil; its taste is nauseous and ethereal, its density 0.932 at 82°.4, its boiling point above 212°; it dissolves in 18 parts of water at 86°.

All these volatile acids are obtained in the same way. The fat oil which they accompany is saponified by an alkali, and the soap decomposed by an excess of tartaric acid, in which the volatile acids are soluble, and may thus be separated from the fat insoluble acids. The volatile acid is then converted into a salt of barytes by adding barytes-water to it, and thus precipitated. The barytic acid is again decomposed by phosphoric or sulphuric acid, and the volatile acid thus set at liberty is rectified by the heat of a water-bath; it is then purified completely from water by means of fused chloride of calcium. These volatile acids form but a small proportion of the butter and oil in which they are found.

Cevadic acid exists in the fat extracted by ether from the seeds of *Veratrum sabadilla*. It forms by distillation a sublimate of white needles of a silky lustre, fusible at 68° (Pelletier and Caventou.) It is named also *sabadillic acid*.

Veratric acid (dried at 212°) $HO + C_{18}H_9O_7$, is obtained by exhausting the seeds of cevadilla by alcohol and sulphuric acid, and neutralising the alcoholic extract by hydrate of lime; veratrine and other products precipitate, but veratric acid remains in solution combined with lime, and is obtained by decomposing its salt of lime with hydrochloric acid. Veratric acid forms short thin quadrangular prisms, colourless and having a slightly acid taste. Its solubility in cold water is small, but it is more soluble in hot water, dissolves easily in hot alcohol and crystallizes on cooling; it is insoluble in ether. The crystals lose water at 212°, and become then of a dull white. They fuse at a high temperature into a colourless liquid, and sublime without residue. Fuming nitric acid and concentrated sulphuric acid have no destructive action on veratric acid (Merck). The alkaline *veratrates* are crystallizable, and very soluble in water and alcohol; the salts of lead and silver are insoluble in water, but soluble in alcohol. *Veratric ether*, $EO+C_{18}H_9O_7$ (Dr. Will), is a crystalline radiated, very friable mass, of density 114.1, fusing at 107°.6 (42° centig.), and imperfectly volatile.

Crotonic acid, termed also Iatrophic acid, is derived from croton oil, the fat oil of the seeds of *Croton tiglium*, in the same way as the preceding acid. It is solid, very volatile and highly poisonous (Pelletier and Caventou).

SECTION V.

OILY ACIDS OF BUTTER OF COCOA, BUTTER OF NUTMEGS, AND PALM OIL.

Cocinic acid, termed also Cocostearic acid, $HO+C_{27}H_{26}O_3$ (Bromeis) is the crystallizable acid of the butter of the cocoanut. This butter is obtained by expressing the dry fruit between hot plates; it is white and possesses the consistence of fat, and is distinguished from other fatty bodies by its great solubility in alcohol.

The mode of preparing cocinic and all the other oily acids is similar. The butter of cocoa is boiled with a solution of an alkali, and thus saponified; the soap is then decomposed by a mineral acid, and the concrete fat acids which appear are expressed repeatedly between folds of blotting paper, till the latter no longer absorbs liquid matter. The expressed solid matter is saponified anew with soda, the soap dissolved in water, and separated by dissolving common salt in the water; the soap thus prepared is again decomposed by tartaric acid. Finally the fat acid thus obtained is purified by crystallizing it repeatedly from alcohol till its point of fusion becomes fixed (Liebig). Cocinic acid is inodorous, of a brilliant white, fuses at 95°, and forms on cooling an amorphous diaphanous mass, like porcelain, is insoluble in water. It may be distilled without change. The *cocinates* of alkaline bases considerably resemble the soaps of the other oily acids.

Sericic or *Myristic acid*, $HO+C_{28}H_{26}O_3$ (Playfair). This acid is obtained from the solid portion of the butter of nutmegs, the fruit of *Myristica moschata*, in which it is combined with glycerine. This solid portion dissolves completely in 4 parts of boiling alcohol, by which it may be easily distinguished from other soluble fat bodies, and gives, on the cooling of the liquid, the sericate of glyceryl in thin silky needles.

Sericic acid, which was discovered by Dr. Playfair, crystallizes in white brilliant plates, of a silky lustre, (hence the name, sericic acid); it fuses between 118°.4, and 120.°2 (48° and 49° centig.), and on cooling becomes a mass, having a very distinct crystalline structure. It is very soluble in alcohol and ether, insoluble in water. It is decomposed by dry distillation, and violently attacked by nitric acid. *Sericates* of alkaline bases are distinguished from other soaps by crystallizing from alcohol; their solutions do not become viscid and thready by concentration, nor are they disturbed by the addition of much water (Playfair). Sericic *ether* is an oily, colourless liquid, of density 0.864. *Sericine*, or sericate of glyceryl, contains as base oxide of glyceryl minus 2HO, or $C_6H_5O_3$; its formula being $C_{118}H_{113}O_{15}$ $=4\ (C_{25}H_{27}O_3)$.

Palmitic acid, $HO+C_{22}H_{31}O_3$ (Fremy, Stenhouse). A soap of the palm oil of commerce yields when decomposed by an acid, a mixture of palmitic and oleic acids; which mixture, dissolved in boiling alcohol, gives crystals of palmitic acid on cooling. Purified by repeated crystallization from alcohol, palmitic acid forms brilliant plates, which completely resemble those of margaric acid, and have the same point of fusion, 140°; it is insoluble in water. It dissolves in alkaline carbonates, and forms a transparent emulsion. After being heated to 572° (300° centig.), palmitic acid does not crystallize from alcohol in leaflets, but in mammillated masses, which, however, have precisely the same composition (Fremy). Palmitic acid distils with very little alteration. Chlorine decomposes the acid when heated, and yields several chlorinated products, which are less fluid, and acid, but do not combine with bases without losing their chlorine. Palmitate of glyceryl or *palmitine*, when pure is crystalline, and of brilliant whiteness, is very slightly soluble in boiling alcohol, but dissolves in boiling ether in all proportions, and is deposited, on cooling, in extremely small crystals. From the analysis of Dr. Stenhouse, palmitine is represented by

$C_{35}H_{33}O_4$, which is anhydrous palmitic acid $C_{32}H_{31}O_3$ plus C_3H_2O; the last formula expressing half an equivalent of anhydrous oxide of glyceryl, $C_6H_7O_5$, from which 3HO have been subtracted.*

Ethalic acid (page 880), termed also cetylic acid, has absolutely the same composition as palmitic acid.

MARGARIC AND STEARIC ACIDS.

Margaric acid, or *Margarylic acid*, $2HO + C_{68}H_{66}O_6 = 2HO + 2(C_{34}H_{33} + O_3)$; in the last formula $C_{34}H_{33}$ represents a radical margaryl (Liebig). This acid forms the principal part of the stearopten, or solid portion of human fat and vegetable fixed oils; it is also produced by the dry distillation of ox and mutton suet, and of stearic acid. It is most easily obtained in a state of purity, by boiling for some minutes stearic acid (the matter composing stearine candles), with an equal weight of nitric acid, of density 1.273 (32° Baumé). The mixture is then left to itself, and after expressing the product, which has become concrete on cooling, between folds of blotting paper, it is crystallized several times successively from alcohol, till its point of fusion remains constant at 140° (60° centig.). It may also be obtained by adding acetate of lead to the solution of a soap of olive oil, or of human fat; on treating the precipitate which falls, by cold or hot ether, margarate of lead remains in a state of purity, being insoluble in that menstruum. This salt gives margaric acid, when heated with a dilute mineral acid. (Liebig's Traité). Margaric acid was so named by Chevreul from its pearly lustre; in external aspect it greatly resembles stearic acid, but is more fusible, the last acid fusing between 158° and 167° (70° and 75° centig).

Margarates.—In the formation of salts of margaric acid, sometimes both its atoms of water, and sometimes only one is replaced by another base. The *ether* of margaric acid, which contains 2 atoms of oxide of ethyl (Varrentrapp), is obtained by saturating with hydrochloric acid gas an alcoholic solution of margaric acid, and withdrawing the excess of hydrochloric acid by washing the product with water. It fuses at 71°.6, is decomposed by alkalies and their carbonates, and also by dry distillation. A mixed soap of oleate and margarate of potash or soda, such as that of olive oil, when dissolved in about eight times its weight of hot water, and the solution afterwards diluted by fifty times its bulk of water, allows an *acid margarate* of potash or soda to precipitate, which may be purified from a little oleate with which it is contaminated by repeated crystallization from alcohol. This salt contains 1 atom of water, and 1 atom of potash as base. Both the acid and neutral margarates of potash crystallize from an alcoholic solution in plates, which have less lustre than the corresponding stearates. *Margarine*, or the margarate of glyceryl, has not been analysed in a state of purity. The solid matter which is formed in olive oil when cold, is a combination of margarate and oleate of glyceryl, according to Pelouze and Boudet.

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* Phil. Mag. 3rd series, xviii, 186.

Stearic acid, hypomargarylic acid, $2HO + C_{68}H_{66}O_5 = 2HO + 2(C_{34}H_{33}) + O_5$.—This acid was discovered by Chevreul, combined with oxide of glyceryl in animal and vegetable fats and in the bile of many animals. It may be obtained pure by crystallizing the stearic acid of commerce from alcohol, till its point of fusion is between 158° and 167°. The latter substance, which forms the stearine candles of commerce, is obtained by saponifying tallow with hydrate of lime, to get rid of its oxide of glyceryl which being set free dissolves in water, and decomposing the insoluble soap of lime with dilute and boiling sulphuric acid. The oleic acid is separated from the stearic acid by submitting the latter to pressure between hot metallic plates. The cake thus obtained is said to contain not more than traces of margaric and oleic acids. Mixed stearic and oleic acids may also be separated by solution in boiling alcohol, from which the stearic acid crystallizes out, and may be purified by successive crystallizations from alcohol.

Stearic acid crystallizes by cooling in white brilliant needles, soft to the touch, pulverisable and insoluble in water. When fused and cast in a mould its surface is rough from crystalline granulation, but if a minute quantity of finely pulverised talc (French white) be mixed with the melted acid, it then solidifies with a perfectly smooth and glossy surface like that of wax. Arsenious acid was improperly used at one time to produce the effect described in stearine candles. Stearic acid fuses at 167°, and solidifies at 158° (Chevreul); its density when solid is 1.01, in the liquid condition 0.854. It is tasteless and inodorous, fused by heat or dissolved in alcohol it reddens litmus; it dissolves in its own weight of ether of density 0.727, when heated in air it burns like wax. Stearic acid is decomposed by dry distillation, and resolved into margaric acid and oxide of margaryl. Nitric acid with heat decomposes it producing first margaric acid, and afterwards suberic and succinic acids. Stearic acid is dissolved entirely by sulphuric acid with a gentle heat, without coloration, and is precipitated on the addition of water in the form of white flocks. It may thus be separated from sulphate of glyceryl, and in a great measure from oleic acid.

Stearates.—Stearic acid is bibasic and forms two classes of salts in which one or both of its basic atoms of water are replaced by a metallic oxide. In the cold, stearic acid only decomposes the alkaline carbonates partially, so as to produce a bistearate and bicarbonate, but with heat it decomposes the same carbonates completely. The neutral stearates of alkaline bases dissolve without alteration in 10 or 20 parts of hot water, but the addition of a large quantity of water causes decomposition, and an acid stearate precipitates while the liquid becomes strongly alkaline; the cooling of a hot solution of a stearate in a small quantity of water is attended with the same decomposition, and causes the whole mass to assume a gelatinous consistence. The *acid* stearate of potash contains $HO+KO$ as base; obtained by precipitation of the neutral stearate in solution by 1000 parts of cold water, and crystallized from alcohol it forms white pearly plates. Boiling water still farther decomposes this stearate, 1000 parts of the former producing with the latter a turbid and viscid liquid, which becomes liquid and transparent at 167°, and deposits pearly plates between 138°.2 and 78°.8 (59° to 26° centig.); 3 atoms of the acid salt are then resolved into 1 atom of the neutral stearate of potash (containing $2KO$ as base) which remains in solution, and into a *bistearate* of potash (containing $KO+3HO$ as base to 2 atoms of acid), which remains in suspension in the liquid. Again, by the cooling of the solution of the neutral stearate of potash, a portion of the former acid stearate of potash is deposited, and half of the alkaline base remains in solution. The precipitate is therefore a mixture of bistearate and acid stearate of potash. If exposed again to boiling water it ends by being converted entirely into bistearate. The solutions of the stearates of alkaline bases are precipitated by salts of all the other metallic oxides, insoluble stearates being formed.

Stearine, or the acid stearate of oxide of glyceryl is the essential part of all kinds of suet; it may be obtained by fusing purified mutton suet by a water bath, dissolving it in 8 or 10 times its volume of ether, allowing the solution to cool, which becomes a thick mass, and washing the expressed solid matter with ether. It forms white pearly plates, fuses at 140° or 143°.6 (60° or 62° centig.), and on cooling again forms a solid pulverisable mass which is not crystalline. It dissolves in 6 or 7 parts of boiling alcohol. This stearate in combination with the oleate of glyceryl forms the solid portion of the butter of cacao. According to the analysis of Liebig and Pelouze, stearine may be represented by $C_6H_7O_5.HO,C_{68}H_{66}O_5+HO$, or by 1 atom of hypomargarylic acid combined with 1 atom of oxide of glyceryl and 1 atom of water as bases, with an additional atom of water of crystallization.

PRODUCTS OF THE DRY DISTILLATION OF MARGARIC AND STEARIC ACIDS.

Stearic acid distilled in a vessel about two thirds filled with the acid, yields first a white solid product, which fixes at 156°.2 (69° centig.), and is a mixture of margaric acid fusible at 140°, of a crystalline neutral body margarone fusible at 170°.6, and of a liquid hydrocarbon in small quantity. The last half of the distilled product is generally softer and accompanied with inflammable gases; and towards the end the residue blackens and assumes the consistence of tar. When stearic acid is distilled with one fourth of its weight of quicklime, a soft buttery mass is obtained, consisting in a great measure of the liquid hydrocarbon and margarone. The products of the distillation of margaric acid are similar. (Redtenbacher and Varrentrapp.)

Margarone, $C_{33}H_{33}O$, was discovered by Bussy. It is formed by the dry distillation of margaric and stearic acids alone or mixed with quicklime; it may be freed from adhering margaric acid by caustic ley in which margarone is insoluble, and purified by crystallization from alcohol. It is a white very friable pearly mass, and becomes electrical by friction. It is volatilised completely from a slip of platinum, but when distilled in a retort it leaves a residue of charcoal. It is soluble in 50 parts of alcohol of 0.837, and in 6½ parts of absolute alcohol, and crystallizes upon the cooling of these solutions. Margarone is also soluble in ether, concentrated acetic acid, oil of turpentine and the liquid fats. Obtained from the distillation of stearic acid and lime, the point of fusion of margarone may rise so high as 186°.8 (86° centig.) after repeated crystallization, it must be then a different substance. From the analyses of margarone fusing at 170°.6 by Bussy, Redtenbacher and Varrentrapp, which agree, it follows that margarone is produced when margaric acid loses the elements of 1 atom of carbonic acid. Margarone is also produced in the distillation of stearic acid, and it is supposed possible by M. Liebig that the carbonic acid may come from the decomposition of the margarone. 2 atoms of hydrated stearic acid, which, indicating $C_{34}H_{33}$ by R, would be $R_4O_{10}+4HO$, are resolved into—

$$\begin{aligned} 3R+9O+3HO &= \text{Margaric acid,} \\ R+O+HO &= \text{Oxide of margaryl.} \end{aligned}$$

Two atoms of oxide of margaryl (a hypothetical compound) would contain the elements of a hydrocarbon $C_{66}H_{66}$, of 1 atom carbonic acid CO_2 and 1 atom of carbon C.

The matter fusible at 186.°8, which Bussy named *stearone* may from his analysis be represented by $2R+O$.

ACID PRODUCTS OF THE ACTION OF NITRIC ACID ON MARGARIC AND STEARIC ACIDS.

When stearic acid is heated with an equal volume of nitric acid of 1.284, an abundant disengagement of deutoxide and peroxide of nitrogen takes place as soon as the mixture boils. If the mixture is then allowed to cool the stearic acid separates apparently unaltered, but really converted entirely into margaric acid, while the nitric acid contains no foreign substance in determinable quantity. By the prolonged action of the boiling acid on margaric acid, the latter is gradually but completely dissolved, and the more readily if the nitric acid be renewed from time to time; the solution then contains suberic acid, succinic acid and an oily substance soluble in nitric acid. (Bromeis.)

Suberic acid, $HO+C_8H_6O_3$.—Brugnatelli first obtained this acid by the action of nitric acid upon cork (page 759). It is prepared by evaporating the solution of stearic or margaric acid in nitric acid to one half and allowing it to rest; the solution in 24 hours becomes a semi-solid mass, which is thrown into a funnel to drain, and washed with cold water. When expressed and crystallized several times it forms pure suberic acid. Suberic acid when humid fuses between 122° and 129°.2 (50 to 54° centig.), but when dried in air or in vacuo, between 244°.4 and 248° (118 to 120° centig.); it is distilled without alteration. Suberic acid is sparingly soluble in cold water, but dissolves in 1.87 parts of boiling water, in 0.87 of boiling alcohol, also in 10 parts of cold and 6 parts of boiling ether. Suberate of lime distilled with an excess of quick-lime gives among other products a colourless liquid, which boils at 374°, and remains liquid at 10.4° (—12° centig.), of which the composition is expressed by C_8H_7O.

Succinic acid, $HO+C_4H_2O_5$; and when sublimed $HO+2C_4H_2O_3$. This acid has long been derived from the distillation of amber (page 904) and exists according to several observers in the resin of some *Coniferæ*. The mother liquor which remains after the separation of suberic acid in the process described above, contains succinic acid soiled with suberic acid. The solution with the washings of the suberic acid is evaporated to crystallization, the product dried and treated with ether in the cold, which easily dissolves suberic acid while it leaves the succinic acid behind in a great measure. The latter may be purified completely by sublimation.

The crystals of succinic acid are colourless and inodorous, of density 1.50, have a somewhat acrid taste, and sublime without decomposition. This acid may be obtained quite anhydrous by several distillations, and then condenses as drops in the receiver. The hydrated acid dissolves in 2 parts of boiling and 5 parts of cold water; it is equally soluble in alcohol and ether. Hydrated succinic acid sublimes at 284°; fuses at 356° losing one half of its water, and boils at 455°. This acid is not sensibly affected by chlorine or nitric acid; added to potash in fusion it gives oxalic acid. Hydrated succinic acid absorbs the

completely from a slip of platinum, but wh osing
retort it leaves a residue of charcoal. It is which
of alcohol of 0.837, and in 6½ parts of
crystallizes upon the cooling of these lts is still
is also soluble in ether, concentrat lly tribasic,
pentine and the liquid fats. Obt t 428° being
stearic acid and lime, the poin ther succinates
rise so high as 186°.8 (86° cen e third atom of
it must be then a different *onia* is much used
margarone fusing at 170° of manganese and other
rentrapp, which agree, d metallic solution must be
when margaric acid erwise the succinate of iron will
acid. Margarone The formula of *succinamide* is NH_2
acid, and it is sa *amide* $NH_2+C_8H_3O_4$. The last com-
acid may co solved in water assumes 2HO, and forms fine
2 atoms of crystals; the solution of these crystals has no
would be metallic salts, and therefore does not contain suc-

SECTION II.

OLEIC ACID AND ACIDS RELATED TO IT.

This acid has been less successfully investigated than stearic acid, and is probably a mixture of two different principles as it is generally obtained. It forms the essential part of the fat oils which are not drying, such as oil of olives and oil of almonds, from the last of which it is most advantageously prepared, and is found in less considerable quantity in tallow, solid fats, human bile and old cheese. The acid derived from a soap of the fat oil of sweet almonds is mixed with its weight of pulverised oxide of lead, and after the mixture is digested on a water-bath for several hours, twice its bulk of ether is added to it, and the whole left to itself for 24 hours. There is thus formed margarate of lead which is insoluble, with an acid oleate of the same base, which is soluble in ether. The ethereal solution is then decomposed by dilute hydrochloric acid, which sets at liberty the oleic acid; the last coming to the surface of the mixture with the ether, and forming an oily limpid stratum. The ether is expelled by evaporation, and the oleic acid saponi-

ali. The soap is purified by dissolving it in water
it by means of common salt; these operations
s repeated. At last, when the soap is colour-
in water and decomposed by tartaric acid;
erated is washed with boiling water, and
Liebig's Traité, ii.). It may be prepared
n the liquid product obtained in the
andles. The formula for oleic acid
entrapp is $C_{44}H_{39}O_4$.

s an oil which is colourless or of a yellowish
very weak odour, an acrid taste, reddens litmus
ly, is lighter than water, and becomes a mass composed of crystalline needles a few degrees above the freezing point of water. It is insoluble in water, but mixes with alcohol of 0.822 in all proportions. Sulphuric acid colours oleic acid. Nitric acid with oleic gives suberic acid, among other products, but no oxalic acid. Peroxide of nitrogen or nitrate of suboxide of mercury transforms oleic acid into elaïdic acid.

Oleates.—Oleic acid decomposes the alkaline carbonates; its compounds are soft, have the appearance of soap and dissolve better in alcohol than in water. *Oleine,* the oleate of oxide of glyceryl, forms the greater portion of the fat oils and of most of the solid fats found in nature. It is mixed in these with margarine or stearine, either of which is deposited in the solid state, when the oil is exposed to great cold, the oleine may then be separated by expression of the solid matter, although never in a state of purity. According to Pelouze and Boudet there are two species of oleine, the liquid portion of such fats as are not drying but disposed to become rancid, differing from the liquid portion of the drying oils, in solubility, and particularly in the transformation which it undergoes under the influence of hyponitric acid into elaidine and elaidic acid, while the oleine of drying oils undergoes no sensible alteration in the same circumstances. The neutral oleate of *potash* is deliquescent in a damp atmosphere, dissolves completely in 4 parts of water, forming a viscid syrup, and is decomposed by a greater excess of water and resolved into potash and an acid oleate of potash. The latter salt is insoluble in water, but dissolves easily in hot or cold alcohol. Oleate of *soda* dissolves in 10 parts of water at 89°.6. Oleate of *lead* is soluble in ether.

Sebacic acid, $HO+C_{10}H_8O_3$. Oleic acid from both the drying and non-drying oils, from tallow and every other source, affords among the products of its dry distillation a matter which becomes concrete on cooling and is sebacic acid, easily recognised by its solubility in water and its property of giving a white precipitate with a salt of lead. This acid is prepared by washing with boiling water the solid and liquid products of the distillation of oleic acid or any of the fats which contain oleic acid, so long as the solution gives crystals on cooling. These crystals are washed with cold water, and crystallized repeatedly from boiling water till they are colourless and free from empyreumatic odour.

Sebacic acid greatly resembles benzoic acid in appearance, and crystallizes in white very light plates or needles of a pearly lustre; it reddens litmus and has an acid taste, loses nothing at 212°, fuses at 260.°6, and sublimes at a higher temperature without alteration. It is but sparingly soluble in cold water, but dissolves easily in boiling water and also in alcohol and ether.

Sebates.—The solution of sebacic acid throws down white precipitates from salts of silver and lead. The sebates of the alkaline bases are very soluble. *Sebacic ether* has been formed in the usual way, by transmitting a stream of hydrochloric acid gas through an alcoholic solution of sebacic acid.

Elaïdic acid, $C_{72}H_{66}O_5$. When a non-drying oil is mixed with nitrate of suboxide of mercury or with peroxide of nitrogen, it gradually becomes solid. This change is due to the transformation of the oleic acid of the oil into elaidic acid, which remains in combination with oxide of glyceryl, forming *elaïdine* or the elaïdate of glyceryl, which is solid and crystalline at the usual temperature. When nitrate of mercury is used in this experiment a portion of the mercury is reduced. To prepare elaïdic acid, peroxide of nitrogen produced by the action of nitric acid on starch is carried through oleic acid free from margaric acid, in a vessel surrounded by cold water. The oleic acid after a time concretes into a mass composed of considerable leaflets, which is washed with boiling water, then dissolved in an equal bulk of alcohol and left to crystallize. Pearly crystals in tables are obtained, which are expressed between folds of blotting paper and crystallized several times from alcohol (Meyer). Elaïdic acid forms thin leaflets of a silvery lustre, considerably resembling benzoic acid. This acid is insoluble in water, sparingly soluble in ether, but highly soluble in alcohol, particularly when hot; the alcoholic solution reddens litmus strongly. Elaïdic acid appears to distil without change. It decomposes alkaline carbonates and forms salts which dissolve in 6 or 8 parts of water, producing a transparent very thick emulsion. These salts may be crystallized from alcohol.

Oleic acid, when treated with nitric acid, gives rise to a series of acid products, discovered by Laurent, many of whose results have since been confirmed by Bromeis. These are, in addition to suberic acid, *azelaic acid*, $HO+C_{10}H_8O_4$, an acid isomeric with suberic acid, and closely resembling it; *pimelic acid*, $HO+C_7H_5O_3$, which crystallizes in white hard grains; *adipic acid*, $HO+C_6H_4O_3$ (Laurent), or $2HO+C_{14}H_9O_7$ (Bromeis); *lipic acid*, when crystallized, $HO+C_5H_3O_4$, when sublimed $C_5H_3O_4$; *azoleic acid*, $C_{13}H_{13}O_4$.

When oleic or elaïdic acid is heated to dryness in a silver capsule with three times its bulk of strong potash ley, the mass being continually stirred till it becomes dry, and heated till the potash begins to fuse, the materials swell considerably, and much hydrogen gas is evolved. The yellowish-brown saline mass contains a new fat acid, besides much acetic acid. This acid, which is the same from both oleic and elaïdic acid, crystallizes when separated in thin needles of brilliant whiteness, fusible at 143°.6 (62° centig.). It has been studied by M. Varrentrapp, who represents it by $HO+C_{32}H_{30}O_3$; which differs only from palmitic and ethalic acids by containing an atom less of hydrogen.

ACIDS OF CASTOR OIL.

Castor oil differs considerably from the other fixed oils, particularly by its solubility in alcohol. A soap of this oil, when decomposed by a mineral acid gives a solid and a liquid oily acid. The first is termed *margaritic acid* by Bussy and Lecanu; it fuses at 266°; the second is named *ricinic acid.*

Nitric acid gives with castor oil an acid, named *œnanthylic acid* by Mr. Tilley, from its relation in œnanthic acid. The formula of œnanthylic acid is $HO+C_{14}H_{13}O_3$ (Tilley). According to Bromeis, œnanthylic acid is identical with the azoleic acid of Laurent.

Castor oil solidifies with nitrate of suboxide of mercury, or with peroxide of nitrogen, and forms a yellow transparent mass like wax. The mass washed with water and dissolved in boiling alcohol furnishes *palmine* in confused crystalline grains. Alkalies saponify palmine like elaïdine, disengaging glycerin, and combining with *palmic acid.* This acid, when pure, crystallizes in white silky needles, grouped about a common centre, is fusible at 122°, and dissolves with facility in alcohol and ether. Palmine and palmic acid are also formed by the action of sulphurous acid gas on castor oil.

ACIDS FORMED BY THE ACTION OF SULPHURIC ACID ON THE FAT OILS.

When sulphuric acid is added in small proportion to fat oils, its action is limited to the abstraction of their glycerin, with which it combines and forms sulphoglyceric acid (page 878), while the oily acids are set at liberty. Such is the reaction that occurs when tallow or hog's lard is mixed with half its weight of sulphuric acid. But when the proportion of sulphuric acid is increased, particular compounds of that acid with the oily acids are produced, which dissolve in water. The compounds thus formed by acting upon olive oil with concentrated sulphuric acid have been carefully studied by M. Fremy.*

Oleic acid and concentrated sulphuric acid combine directly, and form *sulpholeic acid,* a double acid. Pure margaric acid dissolves in sulphuric acid, but does not form a stable compound, for it is separated by water without having undergone any alteration; but when mixed with a certain quantity of oleic acid, both oily acids combine with sulphuric acid, and *sulphomargaric acid* is formed with sulpholeic acid. These two compounds are equally formed, together with sulphate of glycerin, when half a volume of concentrated sulphuric acid is cautiously added by small quantities, to olive oil, any elevation of temperature being guarded against. If then mixed with twice its volume of cold water, and left at rest for twenty-four hours, the sulpholeic and sulphomargaric acids being insoluble in dilute sulphuric come in the form of a syrup to the surface of the liquor, while the sulphate of glycerin remains in the strongly acid liquid below. After the mixture of sulpholeic and sulphomargaric acids is washed with a little water, it is dissolved entirely in a large quantity of water. The solution has an acid and fatty taste, with a bitter after-taste, may be neutralised by an alkali without decomposition, and the salt thus formed occasions in metallic solutions precipitates insoluble in water, and slightly soluble in alcohol.

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* Ann. de Chim. et de Phys. t. lxv, p. 113.

Left to itself, the mixture of sulpholeic and sulphomargaric acid undergoes decomposition; when the solution is made to boil, the decomposition is instantaneous. The sulphuric acid then separates from the elements of the oleic and margaric acids, and these last are themselves transformed into new acids; the margaric acid yielding *metamargaric acid* and *hydromargaritic acid*, the oleic acid, *metoleic acid* and *hydroleic acid*. A compound of hydromargaritic and metamargaric acid, which has the properties of a single acid, has been named *hydromargaric acid*, by Fremy. These compounds are oily bodies insoluble in water, of which those related to margaric acid are solid, and those related to oleic acid liquid at ordinary temperatures. These acids have been also examined by Varrentrapp and by Mr. Miller, but their composition is still involved in considerable uncertainty.

When metoleic and hydroleic acids are distilled, they are decomposed and resolved into two hydrocarbons of the olefiant gas type; *elaëne*, $C_{18}H_{18}$, a white substance, boiling at 230°, and *oleëne*, $C_{12}H_{12}$, a colourless ethereal liquid. Elaëne combines with chlorine, with the evolution of hydrochloric acid, and forms an oily compound (Fremy).

ACROLEINE.

Oils and fats boil at a high temperature, giving off carbonic acid with a little inflammable gas, and a substance possessed of a most pungent odour, which attacks the eyes most painfully, and is named acroleine. The pure oily acids do not yield this substance, but only their compounds with oxide of glyceryl, proving that the acroleine comes from the glycerin. It is, indeed, produced in large quantity by the distillation of pure glycerin. Hence the occurrence of acroleine among the products of the distillation of a fat or oil is a sure and delicate test of the presence of glycerin in the oil.

Acroleine is unknown in a state of purity. It absorbs oxygen with great rapidity from the air and becomes acid. Its solution is decomposed even in close vessels, and yields a tasteless, inodorous, and very indifferent white solid, not resembling fat, and insoluble in all menstrua yet tried. No compound of acroleine has been formed from which it can again be obtained. (Liebig).

CHAPTER IX.

VEGETO-ALKALIES.

In the class of organic bases are included a number of bodies containing nitrogen, which have the properties of the basic or metallic oxides, and form salts with acids. These salts perfectly resemble salts of metallic oxides; the acids which they contain continue to be affected by the usual reagents, sulphate of morphine and sulphate of soda being equally precipitated by chloride of barium, and the organic bases themselves are liberated by stronger bases. Oxide of ethyl and oxide of methyl are likewise bases, but in salts of these, acids have their properties disguised, and can no longer be transferred to other bases such as the metallic oxides, by double decomposition; the compounds of the last mentioned bases with acids diverge therefore widely in their properties from common salts. The present class of organic basis are principally derived from plants, and are known as the vegeto-alkalies. The solutions in water of such of them as are soluble in that liquid, and their solutions in alcohol restore the blue colour of reddened litmus and render yellow turmeric paper brown; they are therefore unequivocally alkaline. The following organic bases appear to be allied to the class of vegeto-alkalies, ammeline, melamine, aniline or crystalline, urea, with certain bases still problematical which Unverdorben derived from volatile animal oil (oil of Dippel), namely odorine, ammoline and animine.

The investigation of this class of bodies was commenced by Derosne, who in 1803 observed narcotine, and by Sertuerner, who, in 1817, recognised in morphine from opium the first vegetable base. These chemists were followed by others, particularly Robiquet and MM. Pelletier and Caventou, who in cinchona bark, nux vomica, and other vegetable matters found organic bases, in which the medicinal virtues of the plants resided. The analogy of these bases to metallic oxides and their valuable applications in medicine have rendered the class a favourite study with both chemists and pharmacians. The method generally pursued in the preparation of such of these bases as, like morphine, are insoluble in water, consists in treating the vegetable substance containing the base with a dilute acid which forms a soluble salt with the base. This solution is concentrated by evaporation, and slightly supersaturated with a soluble alkali, ammonia, hydrate of lime, magnesia or carbonate of soda, by which the vegetable base is precipitated coloured and in an impure condition. To free it from foreign matters, the base or a salt of it is crystallized from alcohol, or if neither the base nor its salt is not much more soluble in hot than in cold alcohol, and therefore does not crystallize well from that liquid, the salt is rendered white by treatment with animal charcoal and repeated crystallization, and the pure base finally precipitated by means of carbonate of soda.

The extraction of bases which are soluble in water and volatile such as conicine, is more difficult. The leaves, flowers, root, or seeds which contain the volatile base are submitted to distillation with a weak solution of caustic alkali. The water which distils over is found to be saturated with the organic base, and generally contains besides a quantity of ammonia resulting from the decomposition of a portion of the former. The distilled water is fully neutralised with dilute sulphuric acid, mixed in a concentrated state with caustic alkali, and the whole digested in a close vessel with ether, which last solvent takes up the liberated vegetable base and the ammonia. The ethereal solution being then distilled by the heat of a waterbath, the ether and ammonia escape, and the vegetable base is left pure in the retort.

Ammonia is a true type of the organic bases in general containing nitrogen. Morphine, quinine, and other members of the class unite directly with hydrochloric acid, as ammonia does, without the separation of water. An atom of water likewise enters into the composition of all their salts containing an oxygen acid, as in the corresponding salts of ammonia. This will appear on comparing together the following formulæ, in which morphine $C_{35}H_{20}NO_6$ appears exactly equivalent to ammonia NH_3:

Hydrochlorate of ammonia, $NH_3 + HCl$.
Hydrochlorate of morphine, $C_{35}H_{20}NO_6 + HCl$.

Sulphate of ammonia $NH_3 + HO,SO_3$
Sulphate of morphine $C_{35}H_{20}NO_6 + HO,SO_3$

Urea even does not form an exception to this rule, but combines directly with hydrochloric acid, according to the observation of Hagen. The hydrochlorates of the vegetable bases also resemble sal ammoniac in forming a crystallizable double salt with one atom of bichloride of platinum, and with two atoms of chloride of mercury, the last corresponding with sal alembroth. This similarity in properties favours the idea that these bases may have a constitution analogous to that of ammonia or be amides of an unknown radical, as ammonia is the amide of hydrogen. The amides derived from most acids are neutral substances, it is true, such as oxamide, $NH_2 + C_2O_2$, succinamide $NH_2 + C_4H_2O_2$, fumaramide, $NH_2 + C_4HO_2$ and benzamide $NH_2 + C_{14}H_5O_2$. Urea, however, which contains two atoms of amidogen, as it is represented by Dumas, $2NH_2 + C_2O_2$ has a basic character; and melamine is strongly basic, which may be represented as $Cy_3 + 3NH_2$, as cyanuric acid is $Cy_3 + O_3$ (Liebig). But although this view of the constitution of vegeto-alkalies is not improbable it must be admitted that the radicals which are thus supposed to be in combination with amidogen, in the vegetable bases, have not been transferred from that to any other radical, much less isolated.

Chlorine transmitted through water containing a vegetable base in suspension quickly produces hydrochloric acid, and forms a hydrochlorate of the base, which is soluble in the water.

This salt is decomposed by the continued application of chlorine, generally with a change of colour in the liquid to yellow or red, and the formation of a precipitate. The precipitate from the salts of strychnine has been found to contain both chlorine and nitrogen. Quinine and cinchonine salts become with chlorine yellow, rose-red, and then violet-red, while a red resinous matter precipitates, which in the air becomes brown, hard, and pulverisable. But the nature of the changes which chlorine produces upon these bases remains still to be investigated. The action of iodine is more definite. According to Pelletier, 2 parts of strychnine and 1 part of iodine dissolved in boiling alcohol, give a precipitate on cooling, of yellow crystalline spangles, resembling mosaic gold, and hydriodate of strychnine crystallizes out from the liquor when concentrated by evaporation. The precipitate appears to contain 1½ equivalent of iodine. The precipitate produced in brucine, treated with tincture of iodine in the same way is yellow; quinine and cinchonine give saffron plates by evaporation of the liquid. The vegetable alkalies are recovered unaltered from these precipitates, when they are treated with a dilute acid, iodine being then liberated or by the action of a solution of caustic potash or soda, and then iodide of potassium or sodium is produced at the same time. The substance thrown down by the action of iodine upon morphine is of a brown colour and differs in nature from the other products as morphine can in no way be revived from it. The hydrogen of the hydriodic acid formed with the other alkalies appears to come from the water, but to be derived in the last case from the decomposition of the vegetable base itself.

Little is known of the action of acids upon the vegetable bases, with the exception of some observations of change of colour which have been made. Thus brucine with a slight excess of nitric acid becomes blood-red, while the colour of pure strychnine is not changed by the same treatment, so that the presence of brucine in strychnine can in this way be detected. Nitric and iodic acids colour morphine, and its salts rose-red. Other bases, such as urea and melamine are decomposed by the stronger acids; urea being converted by the action of concentrated sulphuric acid into carbonic acid and ammonia, by the assumption of two atoms of water; and melamine into cyanuric acid and ammonia, by the assumption of three atoms of water. Thebaine also, exposed to dry hydrochloric acid gas, is resolved into sal ammoniac and a resinous substance having acid properties (Kane); but the other vegetable bases are not found to undergo similar decompositions when exposed to acids.

Curious relations in composition exist between some of the vegetable bases; thus cinchonine and quinine appear only to differ from each other, in the latter containing an atom of oxygen more than the former:

Cinchonine . . . . $C_{20}H_{12}NO$
Quinine . . . . $C_{20}H_{12}NO_2$

Another base, *aricine*, of which the composition is less certainly determined belongs properly to the same group, containing an atom more of oxygen than quinine, that is, $C_{20}H_{12}NO_3$ (Pelletier). These three bases are found together in the quinquinas.

Codeine and morphine, which are found together in opium, appear to have a similar relation in composition to each other:

Codeine. . . . . $C_{35}H_{20}NO_5$,
Morphine. . . . $C_{35}H_{20}NO_6$.

Narcotine from opium and chelidonine, a base likewise from the family of *Papaveraceæ*, appear to be related:

Chelidonine. . . . . $C_{40}H_{20}N_3O_6$ (Will.),
Narcotine. . . . . $C_{40}H_{20}N\,O_{12}$ (Liebig.)

The chelidonine contains 2 atoms of nitrogen more than the narcotine, while the latter contains 6 atoms of oxygen instead of this nitrogen; these being equivalent quantities, it will be remembered of the elements in question. Or, by adding 2 atoms of ammonia to narcotine and subtracting therefrom 6 atoms of water, chelidonine would be produced (Liebig). Attempts, however, which have been made to convert one of these bases into the other have not been successful. But the composition assigned above to narcotine is by no means certain. The formula for the same base deduced by M. Regnault from his analysis is $C_{44}H_{23}NO_{13}$; and that deducible from the atomic weight of its double salt with bichloride of platinum is $C_{48}H_{24}NO_{15}$ (Liebig.)

According to the formulæ which M. Liebig is inclined to adopt for the two bases strychnine and brucine, which also occur together, the latter contains 2 atoms of water and 1 atom of oxygen more than the former:

Strychnine. . . . . $C_{44}H_{23}N_{1\frac{1}{2}}O_5$,
Brucine. . . . . . $C_{44}H_{25}N_{1\frac{1}{2}}O_8$ (Liebig.)

To the same bases M. Regnault assigns formulæ which are somewhat different, but which are equally compatible with the atomic weights of these alkalies as observed in their bichloride of platinum compounds:

Strychnine. . . . . $C_{44}H_{23}N_2O_4$,
Brucine. . . . . . $C_{44}H_{25}N_2O_7$ (Regnault.)

These formulæ indicate the same difference of composition between strychnine and brucine, as do the preceding formulæ for the same compounds. The composition of thebaine from opium, according to the analysis of Dr. Kane is expressed by $C_{25}H_{14}NO_3$. The composition of jervine, a base discovered by M. Simon in the root of *Veratrum album*, and carefully analysed by Dr. Will is $C_{60}H_{45}N_2O_5$.

Several other organic bases have been analysed, but those of which the composition has been already stated are perhaps the only ones, for which we have data to construct formulæ of any considerable degree of probability. The numerical results of the best analyses which have been made of the remaining bases are given by M. Liebig, as follows:*

	ARICINE.	ATROPINE.	CONICINE.	CORYDALINE.
	Pelletier.	Liebig.	Liebig.	Fr. Döbereiner
Carbon. . .	71.0	70.98	66.91	63.05
Hydrogen. .	7.0	7.83	12.00	6.83
Nitrogen. . .	8.0	4.83	12.81	4.32
Oxygen. . .	14.0	16.36	8.28	25.80
	100.0	100.00	100.00	100.00

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* Handwörterbuch der Reinen und Angewandten Chimie, b. i, 709.

	DELPHININE.	EMETINE.	NARCEINE.	
	Couërbe.	Pelletier.	Pelletier.	Couërbe,
Carbon. . .	76.69	64.57	54.73	57.02
Hydrogen. .	8.89	7.17	6.52	6.64
Nitrogen. .	5.93	4.30	4.33	4.76
Oxygen. .	7.49	22.96	34.42	31.58
	100.00	100.00	100.00	100.00

	PSEUDOMORPHINE.	SABADILLINE.	SOLANINE.
	Pelletier.	Couërbe.	Blanchet.
Carbon.	52.74	64.18	62.11
Hydrogen.	5.81	6.88	8.92
Nitrogen.	4.08	7.95	1.64
Oxygen.	37.37	20.99	27.33
	100.00	100.00	100.00

	VERATRINE.		MENISPERMINE.	STAPHISAINE.
	Couërbe.	Dumas and Pellet.	Pellet and Couërbe.	Couërbe.
Carbon. . .	71.48	66.75	71.89	53.57
Hydrogen. .	7.67	8.54	8.01	8.71
Nitrogen. .	5.43	5.04	9.57	5.78
Oxygen. . .	16.42	19.60	10.53	11.94
	100.00	100.00	100.00	100.00

MORPHIA AND THE OTHER BASES IN OPIUM.

When incisions are made in the heads of the white poppy, (*Papaver somniferum*) a milky juice exudes, which is allowed to dry by evaporation on the plant, then scraped off and collected, it forms opium. This drug has been minutely examined, and several vegetable bases derived from it. Its narcotic and anodyne properties are chiefly due to morphine, which is also the base that opium contains in largest proportion.

Morphine or morphia, $C_{35}H_{20}NO_6$.—Much soluble matter is extracted from opium when treated repeatedly in a divided state with water. Most of the narcotine, however remains in the residuum, from which it may be extracted by dilute hydrochloric acid, or by boiling alcohol or ether. If the aqueous solution be greatly concentrated by evaporation, and mixed with a strictly neutral solution of chloride of calcium, a brown impure precipitate of meconate of lime is thrown down, while the bases are converted into hydrochlorates. The liquid being filtered may be made distinctly acid with hydrochloric acid, then digested, in order to discolour it, with pure animal charcoal previously deprived of all phosphate of lime by an acid, filtered again and evaporated for crystallization. A radiated crystalline mass is deposited which consists of hydrochlorate of morphine in combination with hydrochlorate of codeine. This mass may be drained and expressed, then dissolved in hot water, and precipitated by ammonia, which throws down the morphine, while the codeine remains in solution. By farther concentration of the liquid an additional quantity of morphine is deposited; when afterwards an excess of caustic potash is added to the liquid, what remains of the morphine is retained in solution, and the codeine precipitated. Thebaine, narcotine, &c., remain in the former brown mother-liquor, which afforded the crystallized double salt of hydrochlorate of morphine and codeine.

Morphine may be prepared, without reference to the other bases in opium, by various processes, of which the following appears to be the best. The opium is macerated thrice in succession, each time with three parts of cold water, and the mass after each digestion strongly expressed. The liquids are united, raised to the boiling point, and mixed with an equal bulk of milk of lime, the latter containing a quantity of hydrate of lime equal to about one fourth of the weight of the dry opium employed. After boiling for a few minutes the mixture is strained through linen; all the narcotine, meconic acid, &c., remain in the lime precipitate, while all the morphine is contained in the solution in combination with lime. This solution is greatly concentrated by evaporation, then filtered, heated to the boiling point and pounded sal ammoniac is thrown into it, in about the proportion of 1 ounce of sal ammoniac to 1 pound of opium. The caustic lime is thus converted into chloride of calcium, the morphine loses its solvent, and is precipitated in small crystalline needles. Opium yields upon an average a sixteenth of its weight of morphine. (Mohr.)

Morphine as precipitated by ammonia forms a white pulverulent mass, but when crystallized from alcohol it assumes the form of small colourless brilliant prisms. It requires 1000 times its weight of water to dissolve it, but tastes sensibly bitter, and has an alkaline action. Morphine is scarcely soluble in ether, but dissolves in 40 times its weight of cold and in 30 times its weight of boiling alcohol; it is very soluble in caustic alkali. It is fusible by heat, with the loss of water of crystallization, and on solidifying again forms a crystalline mass. Morphine and its salts strike a deep blue colour with the solution of a persalt of iron made as nearly neutral as possible; they likewise decompose iodic acid and liberate iodine, which may then be detected by solution of starch.

Hydrochlorate of morphine crystallizes in needles or feathery crystals, which require from 15 to 20 times their weight of cold water to dissolve them, but dissolve in less than their own weight of boiling water. This, which is perhaps the most valuable of the salts of morphine for medical use, is prepared directly from opium.* *Sulphate* of morphine is highly soluble, and crystallizes like the hydrochlorate. *Bisulphate* of morphine has been formed. *Acetate* of morphine crystallizes with difficulty and is apt to lose a portion of its acid even when kept in crystals; it is much employed in medicine. *Bimeconate* of morphine is a crystallizable salt, in which one of the three atoms of water of meconic acid, is replaced by morphine; this salt also is prepared for medical use; morphine is supposed to exist in opium in combination with meconic acid. The latter acid can easily be detected by re-agents (page 937); and being found in no other vegetable matter but opium, meçonic acid is the substance looked for in testing for opium, of which it is an infallible index.

2. *Narcotine*, $C_{48}H_{24}NO_{15}$, the first crystalline substance derived from opium, is remarkable for its solubility in ether, by means of which it may be dissolved out of opium. It forms colourless brilliant prisms, is tasteless, insoluble in water and caustic alkali, soluble in alcohol. Its solution has no alkaline reaction, but narcotine dissolves in acids; its salts do not crystallize.

3. *Codeine*, $C_{35}H_{20}NO_5$, is remarkable for its solubility in water, being soluble in about 2 parts of boiling water, also in

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* By the process invented by Dr. Robertson and improved by Dr. W. Gregory; Edinburgh Medical and Surgical Journal, Nos. 107 and 111, also Jour. de Phar., xix. 156.

alcohol and ether. It has a weak taste, alkaline reaction, and fuses by the heat of boiling water.

4. *Thebaine* or *paramorphine*, $C_{25}H_{14}NO_3$, is crystallizable, has an alkaline reaction and sharp taste.

5. *Narceine*, a weak base which exists in opium in a very small proportion. Two other bases, *pseudomorphine* and *porphyroxine* have been discovered in certain species of opium. Opium also contains a neutral substance *meconine* in minute quantity, of which the elements are carbon, oxygen and hydrogen only.

QUININE AND CINCHONINE.

Peruvian bark owes its febrifuge qualities to these bases, which it contains in combination with tannic and kinic acids. Quinine is most abundant in *yellow bark*, usually considered as the bark of the *Cinchona cardifolia*, while cinchonine prevails in the grey bark considered as the bark of the *Cinchona nitida* or of the *Cinchona condaminea.*

The ground bark is boiled in water acidulated with hydrochloric acid, the filtered solution mixed with an excess of milk of lime, the precipitate washed, expressed and dried. From this precipitate, which contains quinine, cinchonine, tannate of lime and other matters, the two bases are dissolved out by boiling alcohol; the solution which is strongly coloured is filtered, neutralised with dilute sulphuric acid and the alcohol distilled off. Sulphate of quinine crystallizes on cooling, and is obtained colourless by treatment with animal charcoal and repeated crystallization. The sulphate of cinchonine may be obtained from the coloured mother liquor. Both bases may be isolated by precipitating a solution of their salts in water, by means of ammonia. (Wœhler.)

Quinine, $C_{20}H_{12}NO_2$.—This base is precipitated by ammonia in white flocks, which are not crystalline, and is crystallized even from solution in alcohol with difficulty; but from hot alcohol containing a little ammonia quinine is deposited in fine needles. It is in the state of a hydrate, which fuses about 302° and loses the whole of its water. Quinine is very bitter, alkaline, soluble in 200 parts of boiling water, and highly soluble in alcohol. Most of the salts of this base are crystallizable, intensely bitter and are precipitated by alkalies, bichloride of platinum and oxalic acid.

Subsulphate of quinine, the ordinary sulphate of quinine of the shops, crystallizes in tufts composed of fine needles, which are very light, slightly flexible and have a pearly lustre. It requires 740 parts of water to dissolve it at 55°, but only 30 parts at 212°; it is very soluble in dilute sulphuric acid. It fuses with the appearance of wax, and loses 11½ per cent or 6 atoms of water. The crystallized salt contains 2 atoms of quinine and 8 atoms of water to 1 atom of sulphuric acid. *Neutral sulphate* of quinine is formed by adding a little sulphuric acid to a solution of the sub-sulphate; it crystallizes well in rectangular prisms with rectangular or square bases, is soluble in 11 parts of water at 55°, and fuses in its water of crystallization at 212°. It reddens vegetable blues, although its taste is not perceptibly sour but strongly bitter; it contains 8HO.

Cinchonine, $C_{20}H_{12}NO$.—This base crystallizes readily from alcohol in brilliant prisms. It requires 2500 times its weight of boiling water to dissolve it, and is less soluble in cold water. It is but slightly soluble in cold ether; in its other properties it resembles quinine. *Neutral sulphate* of cinchonine crystallizes also in large octohedral crystals of a rhomboidal base, having a mother of pearl lustre; it contains 8 atoms of water.

STRYCHNINE AND BRUCINE.

These alkalies are derived from the Nux vomica class of plants and particularly from the seeds of *Strychnos nux vomica*, and St. Ignatius' bean, the fruit of *Strychnos ignatia*. To extract them, powdered nux vomica is boiled repeatedly in water, the infusion is concentrated to a syrup and mixed with hydrate of lime in the proportion of 2 ounces of quicklime to 1 pound of the nux vomica. The two bases are contained in the insoluble portion of the mass, which is dried and exposed to boiling alcohol. On evaporating the alcoholic solution strychnine crystallizes first, while the brucine and a portion of strychnine remain in the mother liquor. To complete the separation, the bases in the mother liquor are neutralised by greatly diluted nitric acid, and the nitrate of strychnine crystallized out, while the salt of brucine remains still in solution being much later of crystallizing. From the salts, purified as usual by animal charcoal, and dissolved in water, the bases may be precipitated by ammonia.

Strychnine or *strychnia,* $C_{44}H_{23}N_2O_4$; as obtained from the evaporation of its alcoholic solution it assumes the form of minute colourless octohedrons, composed of two four-sided pyramids, between which a four-sided prism is sometimes interposed. It is soluble in 2500 parts of boiling and in 6667 parts of cold water; but the last solution, weak as it is, has an intensely bitter taste. It is insoluble in absolute alcohol and ether, but sensibly soluble in aqueous alcohol; not fusible. Strychnine acts with great energy on the animal economy, inducing tetanus. Its poisonous action is best counteracted by an infusion of gallnuts or warm tea. The salts of strychnine are generally crystallizable.

Brucine, $C_{44}H_{25}N_2O_7$.—This alkali was first discovered in 1819 by Pelletier and Caventou in the bark of *Brucia antidysenterica.* Brucine greatly resembles strychnine in its properties, acts in the same way on the animal economy but is much less poisonous. It is more soluble in water, and is strongly reddened by nitric acid, while pure strychnine is not.

VERATRINE.

This alkali is found in the seeds of different species of Veratrum, particularly of *Veratrum album* or white hellebore, and *Veratrum sabadilla,* in which it exists combined with veratric acid, (page 955). It is extracted by a process similar to that for strychnine. Veratrine has the aspect of a resin, is friable and gives a white powder; it cannot be crystallized. It is nearly insoluble in water, but dissolves in alcohol and ether. Its taste is excessively acrid and not bitter; with sulphuric acid it becomes yellow, red, and at last violet. Veratrine occasions violent irritation in any mucous membrane to which it is applied, and is highly poisonous. Few of its salts except the hydrochlorate and sulphate are crystallizable; they are not precipitated by bichloride of platinum.

Sabadilline is a crystallizable base which accompanies veratrine in the seeds of Veratrum sabadilla. *Jervine* is another base found in the root of Veratrum album.

CONICINE.

This base is also termed *conia* and *coneine*; its formula is $C_{12}H_{14}NO$. It exists in all parts of hemlock, *Conium maculatum*. It is volatile and is obtained by the distillation of the plant or its seed with a solution of caustic alkali, in the manner formerly indicated. It is a colourless oily liquid, of density 0.89, boiling at 302°; its odour is strong and penetrating, recalling at once that of hemlock and tobacco. The taste of conicine is acrid and corrosive, and it occasions death almost as rapidly as hydrocyanic acid. It is soluble in 100 parts of water, alkaline, miscible with alcohol and ether. With sulphuric, phosphoric, nitric and oxalic acids it forms salts, which crystallize well. Solutions of both conicine and its salts undergo decomposition when air is admitted to them, and become brown with formation of ammonia.

The following organic bases are well established, besides those already enumerated:

Aconitine, in several species of aconitum.

Aricine, in a variety of cinchona bark.

Atropine, in all parts of Atropa belladonna. This base is soluble in water, and is readily decomposed when in solution by heat; it crystallizes in small white prisms. Its taste is most disagreeably bitter and acrid. In a state of solution, and particularly when in combination with acids, it is easily decomposed with the formation of ammonia. It is highly poisonous, and in the most minute proportion possesses the power to dilate the pupil of the eye. The formula for atropine is $C_{34}H_8NO_6$.

Chelidonine and *chelerythrine* in Chelidonium majus.

Colchicine in Colchicum autumnale.

Corydaline in the root of Corydalis bulbosa and fabacea.

Curarine in the Curara poison of India.

Daturine in the seeds particularly of Datura stramonium.

Delphinine in the seeds of Delphinium staphisagria.

Emetine in ipecacuanha, the root of Cephaëlis ipec. It is a white, very fusible powder of a feebly bitter taste, sparingly soluble in water, readily soluble in alcohol; it excites vomiting.

Hyoscyamine in Hyoscyamus niger and albus.

Nicotine exists in the leaves and seed of different species of tobacco, namely Nicotiana tabacum and Nicotiana rustica. It is soluble in water, has the consistence of butter and distils at 284°.

Pelosine in the root of Cissampelos pareira.

Solanine in several species of Solanum, and in the first shoots of germinating potatoes.

The following bases are not so well known and still problematical: apirine, azaridine, blanchinine, buxine, carapine, castine, chioccine, crotonine, cynapine, daphnine, digitaline, esenbeckine, eupatorine, euphorbiine, fumarine, glancine, glaucopicrine, jamaicine, menispermine, paramenispermine, pitayine, sanguinarine, staphisaine, surinamine, violine. Besides two bases in Carthagena quinquina bark and in chinova bark. (Liebig.)

CHAPTER X.

CYANOGEN AND ITS COMPOUNDS.

Cyanogen, NC_2=Cy, which, when free, is a gas (page 428), is remarkable as an organic radical, and enters as a constituent into a large class of compounds. It combines directly with hydrogen, forming a hydrogen-acid, with the whole of the metals forming salts, and is also obtained in combination with oxygen forming several acids, and with chlorine. Cyanogen also appears to be a constituent of urea and uric acid, and of the numerous bodies derived from the decomposition of the latter.

Formation of cyanogen.—This compound is always primarily obtained as a constituent of ferrocyanide of potassium (page 450). In order to explain the reaction between animal matters and carbonate of potash, when fused together at a red heat, which gives rise to that salt, it is necessary to keep in mind the following properties of the salt:—When heated to redness in a close vessel, ferrocyanide of potassium is decomposed into cyanide of potassium, carburet of iron and nitrogen gas; that is, looking upon the ferrocyanide of potassium as a double cyanide, the cyanide of iron is converted into carburet of iron and nitrogen gas, while the cyanide of potassium escapes decomposition. The cyanides of metals in general which can combine with carbon, are decomposed in the same way as the cyanide of iron; thus the cyanide of silver when heated gives at first a little cyanogen, but afterwards it fuses, and glowing suddenly, gives nitrogen gas, the carbon remaining in combination with the silver. The addition of carbonate of potash to the heated ferrocyanide of potassium prevents the decomposition of any cyanogen, cyanide of potassium being then formed, together with oxide of iron; and when charcoal forms a third ingredient of the fused mixture, the oxide of iron is reduced to the metallic state. Hence ferrocyanide of potassium cannot be supposed ready formed in the red-hot mixture of the iron pot in which it is manufactured, that mixture containing both charcoal and carbonate of potash.

In the manufacture of this salt, animal substances, such as dried blood, horn, hoofs, and bristles, with common pearlashes, are the materials employed. The animal matter is used either in its natural state, or it is previously submitted to distillation, as in the preparation of ammonia, and the residual charcoal merely employed for the manufacture of the prussiate. The projection of animal matter into the melted potash occasions a lively effervescence, from the evolution of carbonic acid and some combustible gases. The liquid is stirred after each addition of the materials. The usual proportions employed are equal parts of pearlashes and animal matter, or ten parts of the former and eight parts of carbonised animal matter. Three or four per cent of iron filings are usually added to the mixture. After each addition of animal matter the heat is urged until the whole is fused, and the melted material, which is of a thick consistence, is not removed from the pot until the charcoal is seen to be equally diffused through the whole mass. The mass, after cooling, is placed in an iron pan filled with water, the clear liquid after a time drawn off, and water boiled several times on the insoluble residue. The liquids are evaporated for crystallizing the salt at a temperature not exceeding 203° Fahr. The formation of prussiate takes place after the solution of the melted mass, by the action of the matters dissolved upon the insoluble residue; for this melted mass yields nothing but cyanide of potassium to alcohol, and contains no prussiate. In explanation of the formation of cyanide of potassium in the melted mass, it is stated by Liebig that metallic potassium readily produces that salt when fused with calcined blood, disengaging at the same time a considerable quantity of charcoal; the proportion of nitrogen to carbon, in cyanogen, being one equivalent of the first to two of the last, while in blood, hair, and horn, the proportion is 1 to 6. Now when these animal matters are fused at a high temperature with potash, the free charcoal reduces the potash to the state of potassium; the latter then acts upon the azotised carbonaceous matter, forming cyanogen, with which it unites. A second mode in which cyanide of potassium is produced, is when ammoniacal gas is conducted over a mixture of carbonate of potash and charcoal at a red heat. This is accounted for by the action of ammonia upon charcoal alone at a red heat; the gas is entirely converted into hydrocyanic acid and hydrogen (NH_3 and $2C=H,NC_2$ and $2H$). Now hydrocyanic acid decomposes carbonate of potash at a red heat, forming cyanide of potassium. Hence the product of cyanide of potassium is most considerable when the animal matter is used in its natural state, and not previously carbonised, a fact of which the manufacturers of prussiate of potash have long been aware from experience. To account for the subsequent conversion of the cyanide of potassium in the process into prussiate, it is absolutely necessary that iron exist in the fused mass; but it may indifferently be in the condition of metallic iron, the protosulphuret or the protoxide of iron. The first is readily dissolved by a solution of cyanide of potassium with evolution of hydrogen gas ($3KCy$ with HO and Fe $=2KCy,FeCy$ and KO and H); the second with the formation of sulphuret of potassium, and the third with that of caustic potash. When the iron is added in the state of protosulphate to a solution of cyanide of potassium, one third of the latter salt becomes cyanide of iron (a brown insoluble matter), which is dissolved by the other two-thirds of the alkaline cyanide, and the ferrocyanide formed. These processes are not altered in the slightest degree by mixing caustic potash or its carbonate, or the sulphuret of potassium, with the solution of cyanide of potassium. Much of the iron necessary is derived from the corrosion of the iron pot in which the fusion is conducted.*

HYDROCYANIC ACID.

Syn. *Prussic acid;* formula, H + Cy. This acid was discovered by Scheele, and its constitution first ascertained by Gay-Lussac. It may be obtained anhydrous by transmitting dry sulphuretted hydrogen gas over cyanide of mercury in powder, and contained in a glass tube; sulphuret of mercury being formed, and hydrocyanic acid liberated. The vapour of the latter should be carefully condensed, by conducting it into a Liebig's condenser charged with ice-cold water. It may also be obtained very conveniently by the following process of M. Trautwein. Fifteen parts of ferrocyanide of potassium (page 450) are distilled in a glass retort, at a very gentle heat, with 9 parts of sulphuric acid previously diluted with 9 parts of water and cooled, and the product conducted into a well cooled condenser, containing 5 parts of chloride of calcium in coarse fragments. The distillation is stopt as soon as the salt in the condenser is entirely covered by fluid; and the latter is poured off and transferred into a bottle with a well ground stopper, and secluded from light.

Hydrocyanic acid is a colourless liquid, of density 0.6967 at 64°, still liquid when free from water at —64°, boiling at 80°; miscible with water, alcohol and ether in all proportions. It consists in the state of vapour of 2 volumes of cyanogen and 2 volumes of hydrogen united without condensation; its combining measure is therefore 4 volumes, like that of all other hydrogen-acids; and its theoretical density 943.7, air being 1000. It has a peculiar, very penetrating and suffocating odour, resembling that of the distilled water of bitter almonds, its taste is very bitter and burning. Hydrocyanic acid is in the highest degree poisonous, and its vapour when inspired, produces immediately fatal effects. Its poisonous action is best counteracted by the inhalation of air containing chlorine or ammonia. Hydrocyanic acid scarcely reddens litmus; its vapour is very inflammable. When pure it easily undergoes decomposition, particularly under the influence of light, ammonia being formed with a brown precipitate. This decomposition is prevented by a slight admixture of any other acid. When potassium is heated in the vapour of hydrocyanic acid, cyanide of potassium is formed, and the hydrogen of the acid is disengaged as gas. When its vapour is passed over ignited quicklime or barytes, a mixture of cyanide of the metal and cyanate of its oxide is formed, and pure hydrogen disengaged. Chlorine decomposes hydrocyanic acid, and forms hydrochloric acid and chloride of cyanogen.

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* Liebig; Proceedings of the Chem. Soc. of London, vol. i. p. 2.

The aqueous solution of hydrocyanic acid may be prepared by precipitating potash from cyanide of potassium, by means of tartaric acid, and may in this way be obtained at once of a determinate strength and in a good condition for preservation (page 452). But to prepare this acid in considerable quantity the following process may be followed, which is that of Geiger with the proportions modified. Eight parts of ferrocyanide of potassium with 7 parts of oil of vitriol diluted with 36 parts of water, are slowly distilled nearly to dryness, the product being transmitted through a Liebig's condenser, and collected in a receiver containing at first 8 parts of water. The condensed liquid contains very uniformly 1.62 parts of hydrocyanic acid, which corresponds with one half of the quantity of cyanogen in the salt, the other half of the cyanogen remaining in the residuary insoluble ferrocyanide; the latter is white or yellowish-white when pure, but is often coloured by prussian blue. In this reaction 2 equivalents of ferrocyanide of potassium are decomposed by 6 equivalents of sulphuric acid, which liberate 3 equivalents of hydrocyanic acid. The residuary products are an insoluble ferrocyanide of potassium and iron, $K,Fe+FeCy_3$ (Everitt), and 3 equivalents of bisulphate of potash; or:

$$2(K_2+FeCy_3) \text{ and } 6(HO.SO_3)=K.Fe+FeCy_3 \text{ and } 3(HO,SO_3 \\ +KO,SO_3) \text{ and } 3HCy.$$

If ferrocyanide of potassium be viewed as a double cyanide of iron and potassium, $FeCy+2KCy$, then the decomposition in the foregoing process is limited to the cyanide of potassium of the salt, of which cyanide 3 atoms are decomposed, out of the four contained in 2 equivalents of the double salt; and the residuary insoluble double cyanide is $2FeCy+KCy$.

The proportion of hydrocyanic acid in the acid prepared by the preceding process may be ascertained by accurately weighing a portion of it, amounting to about 100 grains; adding to this portion nitrate of silver in excess, collecting the white insoluble precipitate of cyanide of silver which falls on a weighed filter, drying and weighing together precipitate and filter. Five parts of the precipitate correspond to 1 part of hydrocyanic acid. Or red oxide of mercury may be used to test the strength of the aqueous acid. A drop or two of caustic potash is added to a weighed quantity of the dilute acid, and then a known weight of the red oxide of mercury in fine powder is agitated with it. The metallic oxide dissolves readily as cyanide of mercury, every 4 parts of oxide dissolved corresponding with 1 of anhydrous acid. The hydrocyanic acid may then be reduced to any degree of strength desired, by the addition of water.

The dilute acid, when absolutely pure, soon decomposes, becoming brown and then black, but has stability imparted to it by the smallest trace of sulphuric acid; an addition which should be made when it is intended to preserve hydrocyanic acid for medical use. The solution has the taste, odour and poisonous qualities of the anhydrous acid.

Hydrocyanic acid may be detected by its odour, or by adding a few drops of sulphuric acid to the liquid containing it, and covering the vessel with a glass plate having its lower surface moistened by a solution of nitrate of silver. The hydrocyanic acid rises from its volatility, and produces a white precipitate in the nitrate of silver.

But the most delicate and satisfactory indication of hydrocyanic acid is the production of Prussian blue from it, by a process which is known as Scheele's test. If the liquid to be examined contains much organic matter, as the contents of the stomach in a case of poisoning, it is mixed with about one sixth of its bulk of oil of vitriól and distilled. The test is then applied to the distilled liquid.

1. A few drops of protosulphate of iron are added to the liquid to be tested, with a slight excess of caustic potash so as to precipitate the oxide of iron.

2. The alkaline liquid, after a few minutes' exposure to air,

to allow of the formation of some peroxide of iron, is made acid by the addition of hydrochloric acid, when Prussian blue is formed and precipitates.

Hydrocyanic acid does not decompose carbonates, and may therefore be purified from other acids by distilling it from chalk. But the acid so distilled cannot be preserved without adding a trace of a mineral acid to it.

Cyanides.—Hydrocyanic acid forms a metallic cyanide and water with red oxide of mercury, oxide of silver and other metallic oxides of which the metal has a feeble affinity for oxygen. The cyanides of these metals are not decomposed by dilute oxygen-acids, and resist for a long time the action of concentrated and boiling nitric acid. But the same cyanides are decomposed very easily by sulphuretted hydrogen and hydrochloric acid. The cyanide of mercury is resolved when heated into metal and cyanogen, a portion of the latter remaining in the retort as *paracyanogen*, a black coaly matter, isomeric with cyanogen. Caustic potash is not neutralised by hydrocyanic acid, but remains strongly alkaline, while the solution retains the odour of the acid. Hence it is doubted whether cyanide of potassium is then formed, and rather supposed that hydrocyanic acid unites directly with oxide of potassium. But the solid cyanide of potassium, when dissolved in water, has the same characters as the preceding solution. Cyanide of potassium dissolves the metallic cyanides insoluble in water, forming double salts, and then acquires stability. Cyanide of potassium is decomposed when heated with a solution of caustic potash; the cyanogen of the former salt, uniting with the elements of water, is converted into formic acid and ammonia:

$$K,NC_2 \text{ and } 4HO = KO + C_2HO_3 \text{ and } NH_3.$$

The insoluble cyanides of all the non-alkaline metals may be obtained by adding hydrocyanic acid to an acetate of the metal.

DOUBLE CYANIDES.

The soluble cyanides of potassium and sodium dissolve all the insoluble cyanides of the metals proper, and form double compounds, generally crystallizable, which are not decomposed or modified by alkaline carbonates nor metallic chlorides.

Protocyanide of iron, FeCy, with certain other cyanides, comports itself in a peculiar manner with other metallic cyanides and also with hydrocyanic acid. The cyanide named in combination with two equivalents of cyanide of potassium, $FeCy+2KCy$, forms a neutral salt, *ferrocyanide of potassium*, (page 450), which is not poisonous, gives no hydrocyanic acid with sulphuric acid at the ordinary temperature, while its iron is not precipitated by an alkali or alkaline carbonate; or in this compound the properties of both a cyanide and salt of iron entirely disappear. If the potash of this double salt is precipitated by tartaric acid, a new double cyanide is formed, highly acid and crystallizable, containing protocyanide of iron with 2 equivalents of hydrocyanic acid, $FeCy+2HCy$, known as *ferrocyanic acid*, or *ferrocyanide of hydrogen*. On the view of the constitution of these salts proposed by M. Liebig, they contain a bibasic salt-radical ferrocyanogen $FeCy_3$, in combination, with 2K in the first, and with 2H in the second. Ferrocyanide of *lead*, $2Pb,FeCy_3$, is a white precipitate with a shade of yellow, formed on adding ferrocyanide of potassium to a salt of lead. Ferrocyanide of *copper*, $Cu_2,FeCy_3$, a reddish brown precipitate, insoluble in dilute acids, formed on adding ferrocyanide of potassium to a salt of black oxide of copper. Sesquiferrocyanide of *iron* or *Prussian blue*, $Fe_4,3FeCy_3$, is precipitated on adding the same soluble ferrocyanide to a persalt of iron (page 564). With a protosalt of iron, a greenish white precipitate is produced, which according to Berzelius, is a double ferrocyanide of *potassium* and *iron*, $K.Fe_3,2FeCy_3$ (page 557).

Sesquicyanide of iron, Fe_2Cy_3, in combination with other cyanides, forms another class of compounds, analogous to the preceding. With 3 equivalents of cyanide of potassium, (Fe_2Cy_3+3KCy,) it forms the red prussiate of potash, or ferricyanide of potassium, K_3,Fe_2Cy_6 (page 450). With 3 equivalents of hydrocyanic acid, $FeCy_3+3HCy$, it forms *ferricyanic acid* or *ferricyanide of hydrogen*, H_3,Fe_2Cy_6; it is obtained by decomposing the insoluble ferricyanide of lead by sulphuretted hydrogen. The ferricyanide of potassium produces with a protosalt of iron, ferricyanide of *iron*, Fe_3,Fe_2Cy_6, a beautiful variety of Prussian blue (page 557). The same alkaline ferricyanide does not disturb a persalt of iron.

Sesquicyanide of cobalt, Co_2Cy_3, forms with other cyanides a class of double salts strictly analogous to the immediately preceding class, and which are represented as compounds of a tribasic salt-radical, *cobalticyanogen*, Co_2Cy_6, or as cobalticyanides. *Cobalticyanide of potassium*, K_3,Co_2Cy_6 was discovered by L. Gmelin, and is prepared by heating slightly a mixture of protoxide of cobalt, or its carbonate, with a solution of potash supersaturated with hydrocyanic acid; hydrogen is disengaged with a slight effervescence, and the solution when evaporated, furnishes the salt in question in reddish-yellow crystals, which require to be purified by a second crystallization. It is isomorphous with ferricyanide of potassium.

Sesquicyanide of manganese, Mn_2Cy_3, appears also to form with other cyanides a similar class of salts (page 534).

Sesquicyanide of chromium, Cr_2Cy_3, appears to exist in a class of double cyanides of the same type.

Chromocyanide of potassium, K_3,Cr_2Cy_6, is formed when a mixture of hydrated oxide of chromium with a solution of hydrate of potash to which an excess of hydrocyanic acid has been added, is allowed to evaporate spontaneously in air. The liquid acquires a reddish-brown colour, and deposits yellow crystals, which have a similar form and composition with ferricyanide or cobalticyanide of potassium. (Bœckmann).

Bicyanide of platinum, $PtCy_2$, is considered by Liebig as existing, as a radical, in a series of platinum compounds, discovered by M. Doebereiner. This salt-radical is monobasic. *Platinocyanide of potassium*, $K,PtCy_2+3HO$, is formed on exposing to a heat approaching redness a mixture of equal parts of platinum sponge and dried ferrocyanide of potassium. A solution of the heated mass affords first, when evaporated, crystals of ferrocyanide of potassium, and then of platinocyanide of potassium. The latter crystallizes in thin elongated rhomboidal prisms, which are blue by reflected and yellow by transmitted light. Its solution does not precipitate nitrate of lead, but nearly all the other metallic salts. *Platinocyanic acid* or *platinocyanide of hydrogen*, $H,PtCy_2$ is obtained by decomposing the platinocyanide of mercury suspended in water by a stream of sulphuretted hydrogen gas. It crystallizes in a confused mass, of which the faces reflect a copper lustre; its solution is strongly acid.

COMPOUNDS OF CYANOGEN WITH OXYGEN.

Cyanogen forms the three following isomeric acid compounds with oxygen:

Cyanic acid . . .	$HO,Cy\,O$,
Fulminic acid . .	$2HO,Cy_2O_2$,
Cyanuric acid . .	$3HO,Cy_3O_3$.

Cyanic acid, $HO+CyO$. This acid is formed when cyanogen gas is dissolved in a solution of caustic potash, or passed over carbonate of potash heated to redness; also when ferrocyanide of potassium in a fine powder is ignited in a shallow iron vessel, with stirring and exposure to air at a low red heat. It does not exist except in combination. The hydrated acid was prepared by Wœhler by distilling dry cyanuric acid, and collecting the product in a receiver surrounded by ice.

It is a transparent very volatile liquid, of a pungent odour, highly corrosive, miscible with water. Soon after its preparation this liquid spontaneously undergoes a very extraordinary change; it is converted with the evolution of heat into a white solid matter, *cyamelide*, having the same composition in 100 parts, but insoluble in water and dilute acids, dissolved by caustic alkali, with the formation of ammonia, a cyanate and cyanurate of the alkali. The probable formula of cyamelide is $NH+C_2O_2$ (Liebig). Cyanic acid in solution reddens litmus at first, but is soon transformed into bicarbonate of ammonia, by uniting with the elements of 2 atoms of water:

$$HO+C_2NO \text{ and } 2HO=NH_3,C_2O_4.$$

Cyanates.—The alkaline cyanates are soluble, all the others are insoluble. They are recognised by the decomposition of their acid, which occurs soon after it is liberated by another acid. Ammonia forms two compounds with cyanic acid; one which contains more ammonia than belongs to a neutral salt is produced when the acid vapour and dry ammoniacal gas are mixed together, and forms a white woolly crystalline substance. This cyanate affords ammonia when treated by an alkali, and its acid undergoes the usual decomposition when liberated by another acid. But if heated, either dry or in solution, it loses a little ammonia, still retaining, however, the elements of a neutral cyanate, and is transformed into urea, a change the more remarkable that urea is a substance belonging to the animal economy.

Urea or anormal cyanate of ammonia, $C_2O_2N_2H_4 = C_2O_2 + 2NH_2$ (Dumas). This substance, discovered by Vauquelin and Fourcroy in urine, was obtained from cyanic acid and ammonia by Wœhler, and is the first peculiarly organic product which was formed artificially. It exists in the form of lactate of urea in human urine, and combined with hippuric acid in the urine of the cow and elephant (Cap and Henry). Urea combines with most acids without neutralising them, and is a feeble base.

The following is an advantageous process for urea from human urine, without the use of alcohol. Fresh urine is evaporated in a water-bath to about $\frac{1}{17}$ or $\frac{1}{14}$ of its volume, allowed to cool and filtered. Oxalic acid is taken in the proportion of about half an ounce to each pint of urine employed, dissolved in twice its weight of hot water, and the solution slowly added with continual agitation to the concentrated urine; a large production of a buff-coloured precipitate results, which is oxalate of urea. The impure oxalate, when quite cold, is collected on a large calico filter, slightly washed with a cold solution of oxalic acid, and pressed in the hands as strongly as possible, to get rid of the mother liquor containing salts, &c. The solid mass of oxalate of urea is next dissolved in hot water in a capacious vessel, and neutralised with chalk (whiting) rubbed up with water to a thick cream. So soon as the acid reaction to test-paper ceases, the whole may be thrown on a filter to drain, and squeezed to avoid unnecessary loss. On digesting the solution with animal charcoal, again filtering and concentrating, without ebullition, to a small bulk, crystals of urea are deposited on cooling; these have a brownish colour and disagreeable smell, but by a second solution in warm water, with the addition of a little more bone-black and filtration, the substance is obtained snow-white and inodorous. The urea obtained in this manner burns without sensible ash, and its solution is not troubled by a salt of lime. In the latter part of the evaporation of the first impure solution of urea filtered from the oxalate of lime, insoluble oxalate of lime separates in crusts upon the surface, which must be removed by filtration.

Or, nitrate of urea may be formed by adding to the concentrated urine in a shallow bason an equal bulk of nitric acid of 1.42, taking care by the gradual mixing of the acid and placing the bason in cold water, to prevent any considerable elevation of temperature. This precaution is necessary, for the urine contains chlorides, which when decomposed by the action of nitric acid and heat, produce chlorine and nitrous acid, bodies which re-act injuriously upon urea. The impure nitrate of urea which crystallizes is washed several times with dilute nitric acid, and then dried by placing it upon a clean porous brick or tile, which imbibes the acid liquor. It is redissolved and discoloured by means of animal charcoal, crystallized again, and the solution of colourless nitrate of urea treated with carbonate of barytes or carbonate of potash till perfectly neutralised. The nitrate of barytes or nitrate of potash crystallizes first from the concentrated solution at a low temperature, and the urea afterwards from the mother liquor of those crystals. The urea may be purified from any adhering salt by solution in alcohol and crystallization from that liquid.

Urea may also be prepared in large quantity by decomposing the insoluble cyanate of lead with ammonia or its carbonate.

Urea crystallizes in colourless, flattened, four-sided prisms, is soluble in its own weight of cold water, in 4 or 5 parts of cold alcohol, and in 2 parts of boiling alcohol; it fuses at 248°.

The taste of its aqueous solution is cooling, like that of nitre, acrid and bitter. It is persistent in dry air, but deliquesces in damp air. At a high temperature it undergoes decomposition and produces ammonia, cyanate of ammonia, and solid cyanuric acid. Alkalies give no indication of ammonia in a cold solution of urea, nor is cyanic acid precipitated from it by the metallic salts. The latter acid, however, is revived when a solution of urea is evaporated with nitrate of silver, cyanate of silver being deposited in a crystalline state, and nitrate of ammonia remains in solution. When urea is dissolved in fused potash or in concentrated and boiling sulphuric acid, it assumes the elements of 2 atoms of water, and is converted into carbonic acid and ammonia.

Nitrate of urea is soluble in 8 parts of cold water. It consists of single equivalents of urea, nitric acid and water. (Regnault).

Oxalate of urea crystallizes in long thin prisms, which are much less soluble in water than the nitrate, and have an acid taste. This salt also contains an atom of water. From the oxalate of urea, compounds of urea with other acids may be obtained, by precipitating the oxalic acid with a neutral salt of lime of the other acid, and thus the hippurate, lactate, sulphate, &c. have been formed and crystallized by MM. Cap and Henry.

FULMINIC ACID.

Formula of the acid supposed anhydrous: $C_4N_2O_2=Cy_2O_2$.

Fulminic acid exists in certain fulminating compounds of silver and mercury, discovered by Mr. Howard, but its true nature was first ascertained by Gay-Lussac and Liebig. The acid is bibasic; it undergoes decomposition when separated from bases by a stronger acid, into hydrocyanic acid and other products. Fulminic acid is formed by the action of an excess of nitric acid and alcohol upon nitrate of silver or nitrate of suboxide of mercury. A variety of products result from the mutual action of nitric acid and alcohol, including nitrous acid; 2 atoms of which with 1 atom of ether are resolved, in contact with oxide of silver or mercury, into water and fulminic acid, the last combining with the metallic oxide:

$$\underset{\text{Nitrous acid.}}{N_2O_6} \text{ and } \underset{\text{Ether.}}{C_4H_5O} = \underset{\text{Fulminic acid.}}{C_4N_2O_2} \text{ and } 5HO.$$

Fulminate of silver is also immediately formed and precipitated on transmitting the vapour of nitrous acid through a saturated solution of nitrate of silver in alcohol.

Fulminates.—The salt of *suboxide of mercury* is prepared by dissolving 1 part of mercury in 12 parts of nitric acid of 1.36, by a gentle heat; then adding 11 parts of alcohol of 0.848, and heating by a water-bath. A violent reaction soon occurs, with the escape of nitrous ether vapour, and precipitation of metallic mercury; and soon fulminate of mercury is deposited in white opaque granular crystals, which may be washed when cool, and dried at the ordinary temperature. This salt crystallizes from boiling water in fine, silky needles, and may thus be deprived of the free mercury with which it is accompanied. Fulminate of mercury detonates violently by percussion, or when rubbed between hard bodies; in the flame of a candle it deflagrates with a feeble explosion. Mixed intimately with 6 times its weight of saltpetre, it forms percussion powder, which is introduced in the state of a paste with water, into the copper capsules used with fire-arms. Fulminate of *silver* is prepared like the salt of mercury, but with about twice as much alcohol. It detonates even more violently by percussion than the salt of mercury, and also by heat. This fulminate is deprived of only half its base by an alkali, and a salt formed containing 1 atom of alkali and 1 atom of oxide of silver as bases. Nitric acid throws down an acid fulminate of silver, containing an atom of water as the second base; it is crystallizable and more soluble than the neutral salt. The action of hydrochloric acid upon fulminate of silver is attended with the formation of an acid containing chlorine, *chlorocyanhydric acid*, of which the probable composition is $H_2+C_2NCl_5$ (Gay-Lussac and Liebig).

CYANURIC ACID.

Formula of the acid crystallized from water: $3HO,Cy_3O_3+4HO$.

Cyanuric acid was discovered by Scheele and examined by Serullas, but its true constitution was first ascertained by Liebig and Wœhler. It is formed in a variety of circumstances; in the decomposition of urea by heat, the distillation of uric acid, in the decomposition of the solid chloride of cyanogen by heat, &c. M. Liebig recommends its preparation from Melam (p. 1000). A portion of melam is gently warmed in a little strong sulphuric acid until dissolved; the acid liquid is poured into about 30 parts of water, and boiled in a flask, with the occasional addition of water for four or five days, till the liquid no longer gives a precipitate of ammelide with ammonia. By evaporation the fluid gives brown crystals of cyanuric acid, which may be made colourless by repeated crystallization, or when this fails by dissolving in concentrated sulphuric acid and precipitating by water. The white precipitate by water gives colourless crystals of cyanuric acid from a solution in boiling water. In this process, melam on dissolving in sulphuric acid is transformed into ammonia and ammelide, and the last in contact with the acid diluted with water is resolved into ammonia and cyanuric acid, as expressed in the following equations :

$$\overset{\text{Melam.}}{C_{12}N_{11}H_9} \text{ and } \overset{\text{Water.}}{6HO} = \overset{\text{Ammeline.}}{C_{12}N_9H_9O_6} \text{ and } \overset{\text{Ammonia.}}{2NH_3}.$$

$$\overset{\text{Ammeline.}}{C_{12}N_9H_9O_6} = \overset{\text{Cyanuric acid.}}{C_{12}N_6O_6} \text{ and } \overset{\text{Ammonia.}}{5NH_3}$$

Cyanuric acid has a feeble acid taste, is slightly soluble in cold water and dissolves in 24 parts of boiling water. The crystals from water are oblique prisms of a rhombic base; they contain $4HO$, which they lose in air at the ordinary temperature. Cyanuric acid is obtained anhydrous and crystallized, from a concentrated and boiling solution in nitric or hydrochloric acid. One atom of cyanuric acid is decomposed by dry distillation and resolved into 3 atoms of hydrated cyanic acid, of which it contains the elements. It dissolves with the aid of heat in the concentrated mineral acids, without decomposition, but is decomposed by continued boiling with the formation of carbonic acid and ammonia.

Cyanurates.—In these salts the three atoms of water of the hydrate of cyanuric acid are replaced in whole or in part by metallic oxides. They are all completely decomposed, and their acid liberated by nitric and hydrochloric acids.

Gaseous chloride of cyanogen, CyCl, is most conveniently prepared by passing chlorine in excess into an aqueous solution of hydrocyanic acid, and expelling the chloride of cyanogen by a gentle heat. It is a gas at the ordinary temperature having an insupportable, penetrating odour, and provoking tears. At 0° Fahr., it crystallizes in long needles like spiculæ of ice. It undergoes a metamorphosis if confined liquid in a tube, and deposits the solid isomeric chloride of cyanogen (Persoz). It combines with ammonia, as $CyCl+2NH_3$.

Solid chloride of cyanogen, Cy_3Cl_3, corresponds in constitution with cyanuric acid; it is formed when a mixture of dry chlorine and hydrocyanic acid is exposed to the direct rays of the sun. It is white and sublimes in diaphanous needles. When digested in hot water, it is resolved into hydrochloric and cyanuric acids. It combines also with ammonia, as $Cy_3Cl_3 + 3NH_3$.

Bromide of cyanogen, CyBr, crystallizes in cubes, but is gaseous at 59°.

Iodide of cyanogen, CyI, forms snowy flocks, white and crystalline, which volatilise at 113°.

SULPHOCYANOGEN.

Its formula as it exists in combination is CyS_2; or it is the bisulphuret of cyanogen.

When chlorine is transmitted into a strong solution of sulphocyanide of potassium, a solid matter of a fine yellow colour is precipitated which was considered as sulphocyanogen, but has been shown, by Mr. Parnell, to be different, and named metasulphocyanogen. Sulphocyanogen, as it exists in the sulphocyanide has not yet been isolated.

Hydrosulphocyanic acid, $H + CyS_2$ is obtained by decomposing the basic sulphocyanide of lead by dilute sulphuric acid, and completing the decomposition by sulphuretted hydrogen. It is a colourless liquid of a sour taste, which spontaneously resolves itself in air into several products. It has not been obtained anhydrous. It colours red the solution of a persalt of iron; it is not poisonous.

Sulphocyanides.—The preparation of sulphocyanide of potassium has already been described (page 452). The neutral sulphocyanide of *lead* is deposited in yellow opaque and brilliant crystals, on mixing concentrated solutions of acetate of lead and sulphocyanide of potassium. The basic sulphocyanide, $Pb,CyS_2 + PbO$, on throwing the neutral salt into boiling water, or on adding the tribasic acetate of lead to sulphocyanide of potassium. It is a yellowish white crystalline powder, insoluble in water.

PRODUCTS OF THE DECOMPOSITION OF SULPHOCYANOGEN.

Metasulphocyanogen, $C_{12}N_6S_{12}H_3O$ (Parnell). This is the yellow substance precipitated by the action of chlorine on sulphocyanide of potassium in solution, with formation of chloride of potassium. It is also formed by the action of nitric acid upon the same salt. Metasulphocyanogen dissolves entirely in a solution of caustic potash. An acid added to this solution throws down a lemon yellow precipitate, with a small quantity of a black matter, which has not been fully examined. The yellow substance is the *hydrothiocyanic acid* of Mr. Parnell, of which the probable formula is $C_{10}N_5S_{12}H_6O_2=H_4,Cy_5S_{12}+2HO$. The neutral thiocyanides contain 4 atoms of metal in the place of H_4, and when insoluble are yellow, while the thiocyanides combined with metallic oxide are black.*

Mellon, C_6N_4 (page 428). This is the fixed residue which remains as a yellow powder, on heating dry metasulphocyanogen to low redness in a glass flask, sulphur and bisulphuret of carbon being volatilised at the same time. It was discovered by M. Liebig, who supposed 4 atoms of sulphocyanogen ($C_8N_4S_8$) to be resolved into 1 atom of mellon (C_6N_4) 4 atoms of sulphur (4S) and 2 atoms of bisulphuret of carbon (C_2S_4). But Mr. Parnell has observed the appearance in the decomposition of metasulphocyanogen, of water, sulphuretted hydrogen, and hydrosulphocyanic acid, in addition to the products above. He supposes three equivalents of metasulphocyanogen to be resolved into four of mellon, $C_{24}N_{16}$; two of hydrosulphocyanic acid, $S_4C_4N_2H_2$; four of sulphuretted hydrogen H_4S_4; eight of bisulphuret of carbon, C_8S_{16}; twelve of sulphur S_{12}, and three of water H_3O_3.

Mellon is insoluble in water, alcohol, and dilute acids; is decomposed at a bright red heat into three volumes of cyanogen and 1 volume of nitrogen. It is a salt-radical, combining directly with potassium, with ignition and formation of *mellonide of potassium*; with hydrogen it forms *hydromellonic acid*.

Cyanilic acid, $C_6N_3H_3O_6$ (Liebig). Mellon is decomposed by the prolonged action of boiling nitric acid, with disengagement of gas, and the liquid yields on evaporation, colourless, anhydrous octohedrons of cyanilic acid, which has the same composition as cyanuric acid, and also crystallizes from water with 4HO. The nitric acid after its action on mellon contains ammonia; it is the only acid which causes mellon to undergo this transformation.

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* Philosoph. Mag. 3rd. Series, vol. 17, p. 249.

Boiling potash ley dissolves mellon with evolution of ammonia and formation of a salt in white needles, which has not been sufficiently examined.

Hydro-persulphocyanic acid, CyS_3H (Woskresensky;) a yellow matter insoluble in water, formed when sulphocyanide of potassium heated to fusion is exposed to a stream of dry hydrochloric acid. It is soluble in boiling alcohol.

Melam, $C_{12}N_{11}H_9$ (Liebig), one of the products of the decomposition by heat of sulphocyanide of ammonium. It is most conveniently prepared by heating a mixture of dry sulphocyanide of potassium with twice its weight of sal ammoniac in a porcelain bason, above 350° or 400°, by a charcoal chauffer. Ammonia, sulphuretted hydrogen and bisulphuret of carbon go off, and melam remains mixed with chloride of potassium, from which it may be separated by washing with pure water. Melam is a greyish white powder, not crystalline, insoluble in water, alcohol, and ether. It is decomposed by heat into mellon and ammonia.

Melamine, $C_6N_6H_6$ (Liebig); a salifiable base formed by dissolving melam in 1 part of hydrate of potash dissolved in 20 parts of water; the mixture being kept in ebullition till the turbid liquor becomes perfectly clear. One atom of melam with 2 atoms of water are then resolved into 1 atom of melamine and 1 atom of ammeline. Melamine is deposited from the concentrated solution on cooling in anhydrous rhomboidal octohedrons, transparent, colourless or tinged slightly yellow. It is very slightly soluble in cold water, dissolves to a greater extent in boiling water, but its solution is very slowly effected; it is neutral to test paper, insoluble in alcohol and ether. When dry melamine is strongly heated, the greater portion of sublimes without decomposition. Melamine forms crystallizable salts on combining with dilute acids.

Ammeline, $C_6N_5H_5O_2$ (Liebig). The alkaline solution above, from which melamine crystallizes, still contains ammeline dissolved in caustic potash, from which it is obtained, on neutralising with acetic acid, as a gelatinous white precipitate, this is washed and then redissolved in dilute nitric acid; the solution gives by evaporation crystals of pure nitrate of ammeline, from which, dissolved in water, pure ammeline is precipitated by carbonate of ammonia. It may also be obtained by dissolving melam in dilute and boiling hydrochloric acid.

Ammeline forms very fine brilliant silky needles; is insoluble in water, alcohol, and ether, but dissolves in caustic alkalies. Ammeline is a feeble base and combines only with the more powerful acids. Its salts are crystalline, have an acid reaction, and water precipitates ammeline from them.

Ammelide, $C_{12}N_9H_9O_6$ (Liebig), is a product of the decomposition of melam, melamine, and ammeline by concentrated acids. The solution is treated with alcohol, and the precipitate of ammelide washed with cold water. It may be purified by solution in nitric acid and precipitation by carbonate of ammonia. It is a white powder insoluble in water, alcohol, and ether; soluble in alkalies and the stronger acids. It forms a crystalline compound with nitric acid, which is decomposed by water. When long boiled in dilute nitric or sulphuric acid, ammelide is completely decomposed and converted into ammonia and cyanuric acid.

Hydrosulphurets of cyanogen.—Dry sulphuretted hydrogen and cyanogen do not combine when mixed together over mercury, but if a drop of water is added, the gases are condensed in the water, which affords thin yellow crystals by evaporation, observed by Gay-Lussac, of which the composition is $C_4N_2H_3S_3$; or an allantoin, in which the oxygen is replaced by sulphur (Vœlckel). When a stream of sulphuretted hydrogen is conducted into an alcoholic solution of cyanogen, the liquid soon becomes yellow, and deposits fine orange red crystals, when artificially cooled, discovered by Wœhler, of which the composition is $C_2NHS + HS$; its compound with lead $C_2NHS + PbS$ (Vœlckel).

Sulphocyanhydric acid and sulphuretted hydrogen.—A compound acid of these acids was obtained by Zeise, as one of the products of the reaction between gaseous ammonia and the bisulphuret of carbon in alcohol. Its empirical formula is CyS_3H_2

URIC ACID AND THE PRODUCTS OF ITS DECOMPOSITION.

These form a well defined class of compounds, which appear from their analysis to contain cyanogen and carbonic oxide. M. Liebig connects the different members of the class by supposing them to contain a compound radical in common, *urile*, which is itself a combination of 2 atoms of cyanogen and 4 atoms of carbonic oxide. Urile, $2Cy+4CO=C_8N_2O_4$, being indicated by Ul, then the compounds are represented by the formulæ:—

Rational formulæ.		Empyrical formulæ.
$2Ul+1$ atom urea	=Uric acid	$=C_{10}N_4H_4O_6$
$2Ul+O_2+4HO$	=Alloxan	$=C_8N_2H_4O_{10}$
$2Ul+O+5HO$	=Alloxantin	$=C_8N_2H_5O_{10}$
$2Ul+1$ atom ammonia $+2HO$	=Uramile	$=C_8N_3H_5O_6$

URIC ACID.

Formula, $C_{10}N_4H_4O_6$, or $2Ul+(C_2O_2+2NH_2)$. An acid which exists in the urine of all carnivorous animals, and forms the basis of most urinary concretions. It forms in combination with ammonia, the white part of the excrement of birds; and vast accumulations of that urate exist in the *guano*, or decomposed excrement of aquatic birds, by which many of the small islands on the coast of Peru and Chili are covered, and which is used as manure.

Uric acid is conveniently prepared from the chalk-like excrement of serpents. The solid urine of the Boa is reduced to fine powder and added to a boiling and very dilute solution of potash, sufficient only for the solution of a portion, and ebullition continued until the undissolved mass appears quite white.

The whole is then allowed to cool, thrown upon a calico filter, and washed until the water passes off very nearly colourless. The washed white mass, which consists of urate of potash, is next dissolved in another portion of caustic alkali, filtered, and slowly added to an excess of dilute hydrochloric acid maintained in a state of ebullition. The uric acid which precipitates, may be washed first by decantation, and afterwards more completely on a filter, and is obtained perfectly white. From the brown liquid filtered from the urate of potash, an additional quantity of uric acid may be obtained by supersaturation with hydrochloric acid, but the product has a brownish colour.

Uric acid crystallizes in thin scales of a silky lustre and brilliant whiteness, is inodorous and insipid, loses nothing at 212°. This acid is nearly insoluble in cold water, requiring, according to Prout 10,000 parts of water at 60° for solution, and but slightly soluble in hot water; its solution has a feeble reddening effect upon litmus. It is insoluble in alcohol and ether. It dissolves in concentrated sulphuric acid, and is again thrown down on dilution with water. It is also more soluble in concentrated hydrochloric acid than in water. In nitric acid, uric acid dissolves with lively effervescence, the gases disengaged being carbonic acid and nitrogen in equal volumes. The solution contains alloxan, alloxantin, urea, parabanic acid and ammonia. The concentrated liquor becomes of a purple red (from murexide), when an excess of ammonia is added, affording a character by which uric acid may be recognised. (Liebig).

Urates.—Metallic oxides appear to combine with uric acid without displacing the basic water of the acid which remains in the salt. The urates of the alkalies and alkaline earths are sparingly soluble in cold, but more freely soluble in boiling water. Urate of ammonia dissolves, according to Dr. Prout, in 480 parts of water at 60°. Urate of potash forms crystalline scales soluble in about 500 parts of cold water, but is much more soluble in boiling water, especially if there be an excess of alkali present. All the urates are decomposed by acetic acid. Urate of soda forms the principal constituent of gouty concretions.

ALLANTOIN.

Formula: $C_4H_3N_2O_3$, or Cy_2+3HO (Liebig and Wœhler). This is a crystalline substance found in the allantoic fluid of the cow, and produced artificially by boiling uric acid with the puce-coloured oxide (peroxide) of lead. It is deposited from the allantoic fluid of the cow when concentrated by a gentle heat to one-fourth of its bulk, upon cooling, in crystals, which are treated with animal charcoal and obtained perfectly pure.

In the artificial process for allantoin, 1 part of uric acid is boiled in 2 parts of water, and the puce oxide of lead added in small qualities so long as it changes colour. The liquid, filtered boiling, and concentrated by evaporation, deposits allantoin in crystals, which are purified by repeated crystallizations. In the formation of allantoin, 2 atoms of the puce oxide of lead lose the half of their oxygen, which, with 3 atoms of water, produces 2 atoms of oxalic acid, 1 atom of allantoin and 1 atom of urea:

$$\begin{array}{c}
\left.\begin{array}{llll} & C_4O_4+N_2C_4 & & =1\text{ at. Urile} \\ 2PbO+ & O_2 & H_3O_3 & +1\text{ at. Urea} \end{array}\right\}=1\text{ at. uric acid.} \\
\hline
\text{2 atoms of oxalate of lead} \quad +1\text{ at. of allant.} \quad +1\text{ at. of urea.}
\end{array}$$

Allantoin crystallizes in brilliant colourless prisms derived from a rhombohedron. It is tasteless, neutral to test paper, soluble in 160 parts of cold and in less boiling water. It dissolves in nitric acid; the solution is decomposed by ebullition, without the disengagement of ruddy fumes. It also dissolves in a hot solution of an alkali or alkaline carbonate, and crystallizes from these solutions without change. Allantoin contains the elements of anhydrous oxalate of ammonia, minus 3 atoms of water, which explains its conversion by boiling alkalies into oxalic acid and ammonia. A solution of allantoin in water at the boiling temperature, to which a few drops of ammonia is added, gives a white precipitate with nitrate of silver, of which the composition is expressed by $C_8N_4H_5O_5+AgO$ that is, 2 atoms of allantoin, $C_8N_4H_6O_6$, in which 1 atom of water is replaced by 1 atom of oxide of silver. Allantoin has also been named allantoic acid.

ALLOXAN.

Formula, $C_8N_2H_4O_{10}$. It is the erythric acid of Brugnatelli, and was discovered by Liebig and Wœhler in the decomposition of uric acid.

They recommend for its preparation, to add uric acid gradually to nitric acid of 1.35, by which it is dissolved with effervescence. "The action must be gentle, and, if heat be applied, it must be done cautiously. As soon as crystals begin to appear in the warm liquid, no more uric acid is added for the present, and the whole is allowed to cool, when it becomes semi-solid from the separation of crystals of alloxan. The mass is thrown on a funnel stopped with a little asbestos, and, when it has ceased to drop, the acid liquor remaining in the crystals is carefully displaced by a little ice-cold water. The crystals are purified by solution in water, avoiding a strong heat, and by recrystallization. The acid liquid which has drained from the first crystals is again treated as above with uric acid, and in this way one portion of nitric acid may be made to yield 4 to 5 drops of crystals of alloxan. The mother-liquor finally left is not lost but yields a large quantity of parabanic acid, oxalurate of ammonia, or murexide, if properly treated. By this process Gregory obtains, from 100 parts of uric acid, 65 parts of anhydrous alloxan equal to at least 90 of the hydrated crystals." (Turner's Elem. of Chem. by Liebig and Gregory).

Alloxan crystallizes in large colourless octohedrons of a rhombic base, having considerable lustre; they contain 6 atoms of water and are efflorescent. A saturated hot solution gives alloxan on cooling in oblique rhomboidal prisms, which are anhydrous. It is very soluble in water, reddens vegetable colours and stains the epidermis purple. It is converted by the action of acids into alloxanic acid, and when boiled with an alkali, it is transformed into urea and mesoxalic acid. The puce oxide of lead changes it, with the aid of heat, into urea and carbonate of lead, mixed with some traces of oxalate of lead. It is transformed into alloxantin by sulphuretted hydrogen, by protochloride of tin, or by metallic zinc with hydrochloric acid. An excess of ammonia transforms it into mycomelinic acid, nitric acid into parabanic acid, sulphuric acid or hydrochloric acid into alloxantin, sulphurous acid and ammonia into thionurate of ammonia, alloxantin and ammonia into murexide (Liebig).

Alloxanic acid (supposed anhydrous), $C_4N_2HO_4$; is produced by the metamorphosis of alloxan by caustic alkalies. The anhydrous acid contains the elements of half an atom of alloxan minus 1 atom of water.

Mesoxalic acid (hydrated), $4HO+C_6O_9H$; or rather, $2HO+C_3O_4$, is one of the products of boiling a saturated solution of alloxanate of barytes or strontian. Also, when a solution of alloxan is poured drop by drop into a boiling solution of acetate of lead, a granular very heavy precipitate of mesoxalate of lead falls, while nothing remains in the acid liquor but the excess of acetate of lead and pure urea. Both this and the preceding acid may be separated and crystallized, and are powerful acids.

Mycomelinic acid, $C_{16}N_8H_{10}O_{10}$, is formed on adding an excess of ammonia to a solution of alloxan, and raising the mixture to the boiling point. It is almost insoluble in cold water, and is thrown down as a yellow gelatinous precipitate, which becomes a yellow porous powder on drying.

Parabanic acid, $2HO + C_6N_2O_4$, is one of the products of the decomposition of uric acid or alloxan by nitric acid, discovered by Liebig and Wœhler. It is prepared by dissolving 1 part of uric acid or alloxan in 8 parts of nitric acid of ordinary strength, evaporating the liquor to a syrup, and allowing it to crystallize.

It forms thin, transparent, six-sided prisms, of a very sour taste, resembling that of oxalic acid. It is very soluble in water and does not effloresce in the atmosphere nor by heat; it is partially volatile.

Oxaluric acid, $HO + C_6N_2H_3O_7$, is formed on adding ammonia to a boiling solution of parabanic acid, or on supersaturating with ammonia a solution recently prepared of uric acid in nitric acid, which yields by evaporation crystals of oxalurate of ammonia. The acid when separated is a brilliant white powder, light and crystalline; its taste is very sour, and it reddens litmus. Its aqueous solution is decomposed completely by ebullition, and resolved into oxalic acid and oxalate of urea. It is formed by the combination of the elements of parabanic acid with 2 atoms of water. The crystallized acid contains the elements of 2 atoms of oxalic acid and of 1 atom of urea, and may be considered as uric acid in which the urile is replaced by oxalic acid. (Liebig).

Thionuric acid, $HO + C_8N_3H_5O_6(S_2O_6)$, is a bibasic acid produced by the simultaneous action of sulphurous acid and ammonia upon alloxan. Liberated from thionurate of lead by sulphuretted hydrogen, it crystallizes in very thin needles, is persistent in air, very soluble in water, and has an acid taste. It contains the elements of 1 atom of alloxan, 1 atom of ammonia and 2 atoms of sulphurous acid. On heating thionuric acid, 2 atoms of oxygen of the alloxan re-unite with 2 atoms of sulphurous acid to form sulphuric acid, while the elements of urile, ammonia and water combine and give rise to uramile.

Uramile, $C_8N_3H_5O_6$, is prepared by adding hydrochloric acid to a saturated and boiling solution of thionurate of ammonia, till it is strongly acid; the heat is continued till the liquid begins to become turbid; it is then allowed to cool for crystallization. Uramile crystallizes in thin and hard tufts, or presents itself in the form of a brilliant white powder, composed of very thin silky needles. It is sparingly soluble in hot water, wholly insoluble in cold water, dissolves in ammonia and caustic alkalies, and is again precipitated, without alteration, by acids. A solution of potash and dilute acids boiled upon uramile, convert it into uramilic acid, disengaging ammonia. The ammoniacal solution of uramile becomes purple-red in air, and deposits crystalline needles of a green colour and metallic lustre. In contact with oxide of mercury or oxide of silver, it is decomposed, by ebullition, into murexide, and at the same time reduces the oxides to the metallic state.

Uramilic acid, $C_{16}N_5H_{10}O_{15}$, is prepared by dissolving thionurate of ammonia in cold water, adding to the saturated solution a small quantity of sulphuric acid, and evaporating by a water-bath; after a time uramilic acid is deposited in transparent, four-sided prisms of a vitreous lustre, or in silky needles. It is soluble in 6 or 8 parts of cold water, and in 3 parts of boiling water; the solution is feebly acid. In the formation of uramilic acid 2 atoms of uramile unite with the elements of 3 atoms of water, yielding up at the same time the elements of 1 atom of ammonia.

ALLOXANTIN.

Formula: $C_8N_2H_5O_{10}$. Alloxantin was first observed by Dr. Prout among the products of the decomposition of uric acid by nitric acid, and more lately produced and studied by MM. Liebig and Wœhler. Several processes are given by the latter chemists for its preparation. 1. *From uric acid.*—One part of uric acid is boiled with 32 parts of water, and dilute nitric acid added by small portions at a time till the uric acid is completely dissolved, and the liquor evaporated to two-thirds. In the course of a few days, or sometimes a few hours, the alloxantin is deposited in crystals, which are purified by new crystallizations. 2. *From alloxan.*—It is produced in large quantity by carrying a stream of sulphuretted hydrogen into a solution of alloxan. Sulphur is first deposited, and then the whole becomes a thick mass of crystals of alloxantin, which are separated from sulphur by solution in boiling water. The alloxantin crystallizes by evaporation in a state of purity. 3. On exposing a solution of alloxan to the action of the voltaic battery, oxygen is evolved at the zincoid, and alloxantin is deposited on the chloroid in crystalline crusts.

Alloxantin crystallizes in oblique prisms of four sides, which are colourless or slightly yellow, hard and easily reduced to powder; they become red in air impregnated with ammonia and acquire a green metallic lustre. They are not altered at 212°, but at 302° (150° centig.) lose three atoms of water; are sparingly soluble in cold water, more soluble in boiling water; the solution reddens litmus. Alloxantin heated in chlorine-water, or in strong nitric acid, is changed into alloxan; with salts of silver, it produces a black precipitate of metallic silver. It is decomposed by alkalies; barytes-water produces in its solution a violet precipitate, which is made colourless by heat, and in the end disappears entirely. By the action of boiling sulphuric acid, 2 atoms of alloxan are converted, with the concurrence of 2 atoms of water, into 1 atom of alloxantin, 3 atoms of oxalic acid, 2 atoms of ammonia, and 2 atoms of carbonic acid.

The circumstances of the formation of alloxantin are thus explained by M. Liebig. By the action of nitric acid, the urile of the uric acid combines with 1 atom of oxygen and with the elements of 5 atoms of water, giving rise to 1 atom of alloxantin and to peroxide of nitrogen, NO_4, which in contact with water is converted into nitrous and nitric acids; the nitrous acid is decomposed with half of the urea set at liberty, while the other half of the urea forms with nitric acid, nitrate of urea. In the process again with sulphuretted hydrogen, 1 atom of oxygen of the alloxan combines with hydrogen from the sulphuretted hydrogen to form water which remains in the constitution of the alloxantin; the sulphur set free is deposited.

Products of the decomposition of alloxantin.—When a stream of sulphuretted hydrogen is carried into a boiling solution of alloxantin, more sulphur is deposited, and on saturating with ammonia a salt crystallizes in thin colourless needles, of which the formula is $C_8N_3H_7O_8$, which is considered a compound of a new acid, *dialuric acid*, with ammonia. This acid is resolved into new products when liberated by another acid, one of these produced by exposure to air and evaporation of the solution of the ammoniacal salt in dilute sulphuric or hydrochloric acid, is *dimorphous alloxantin*, a body having the same composition as alloxantin but a different form. On mingling boiling solutions of sal ammoniac and alloxantin, the mixture becomes suddenly of a purple red colour, then gradually loses its colour, becoming turbid, and deposits colourless brilliant plates of uramile, which become rose-red on drying. The liquid contains, after its decomposition, alloxan and free hydrochloric acid. When a solution of alloxantin is heated with caustic ammonia, uramile and mycomelinate of ammonia are first formed, but are decomposed into other products by the prolonged action of ammonia and air. A recent solution of alloxantin in ammonia gradually absorbs oxygen from the air, and deposits crystals of oxalurate of ammonia.

MUREXIDE.

Formula: $C_{12}N_5H_6O_8$ (Liebig and Wœhler). This beautiful product of the decomposition of uric acid was first described by Dr. Prout, under the name of purpurate of ammonia. Murexide may be formed by evaporating a solution of uric acid in dilute nitric acid, until the solution acquires a flesh red colour, allowing it to cool to 160°, and then treating it with a dilute solution of ammonia, till the presence of free ammonia is remarked by the odour; the liquid is then diluted with half its volume of water and allowed to cool. It may also be formed by bringing together many of the products of the action of nitric acid on uric acid, with ammonia, with or without the presence of atmospheric air. The following method, proposed by Liebig and slightly modified by Gregory, appears to be the easiest and most certain, and also most productive.

"Seven grains of hydrated alloxan and 4 grains of alloxantin are dissolved by boiling in 240 grains of water, and the boiling solution added to 80 grains by measure of a cold and strong solution of carbonate of ammonia. This mixture has precisely the proper temperature, and deposits very fine crystals of murexide. The experiment is not so successful on a large scale, probably because the liquid, by remaining longer warm, undergoes a partial change. It is best to try first a saturated solution in cold water of carbonate of ammonia. If it do not yield good crystals, add a little water, and try it again, and so on till a solution of the carbonate is obtained, which gives a good result. The difficulty is owing to the spontaneous formation of different carbonates by the action of water on the carbonate of the shops; but when a proper solution is obtained, the experiment never fails." (Turner's Chem. &c. p. 776).

Murexide crystallizes in short four-sided prisms, of which two faces, like the upper wings of cantharides, reflect a green metallic lustre. The crystals are garnet-red by transmitted light; their powder is reddish brown, and acquires a green lustre under the burnisher. Murexide is but slightly soluble in cold water, but colours it of a magnificent purple; it dissolves, however, readily in water at 158°, and crystallizes again on the cooling of its solution; it is insoluble in alcohol, ether, or in water saturated with carbonate of ammonia. But this substance cannot be purified or obtained in crystals of large size, by crystallizing it from boiling water. For on boiling murexide in a small quantity of water for the time necessary to dissolve the whole, the crystals become colourless, and upon cooling, a yellow gelatinous matter precipitates. Hence, probably, the slight uncertainty which attends even the best process for the preparation of this substance. Murexide dissolves in solution of potash, producing a superb indigo blue colour, which disappears with the application of heat, ammonia being disengaged. All the inorganic acids decompose murexide, precipitating from its solution murexan in small brilliant plates. Sulphuretted hydrogen decomposes it immediately into alloxantin, dialuric acid and murexan, while sulphur is set free.

Murexan, $C_6N_2H_4O_5$, was named purpuric acid by Prout. It is formed on dissolving murexide with heat in caustic potash, heating till the blue colour disappears, and then adding an excess of dilute sulphuric acid. It crystallizes in colourless plates, which have a silky lustre and are very brilliant, is insoluble in water and dilute acids; it dissolves in ammonia and other alkalies, in the cold, without neutralising them. The properties of murexan closely resemble those of uramile. Like uramile, murexan boiled with water, red oxide of mercury and a little ammonia, yields murexide. The composition of murexan and uramile, also, not differing much in 100 parts, Dr. Gregory admits it to be possible that these two substances may be essentially the same.

CHAPTER XI.

SECTION I.

ORGANIC PROCESSES OF PLANTS AND ANIMALS.

Without describing the structure of the organs of plants and animals, I may state shortly the principal observations which have been made respecting the food of plants and animals and the chemical changes which it undergoes in the animal economy, with the relation which subsists between plants and animals. Besides secreting the lignin and cellulose which form the basis of their own solid structure, plants elaborate in their organs various substances destitute of structure, such as sugar, starch, gum, resins, essences, fat oils, and the endless variety of principles which the vegetable kingdom presents to the chemist for examination. These principles are either contained in the fluids of the plant, or are stored up in particular organs, or are thrown off as excretions.

The mode of formation of such principles in the plant and the chemical agencies by which one principle is transformed into another, have hitherto been very imperfectly traced, owing to the difficulty of the investigation occasioned both by the minuteness of the mechanism aud the obscure nature of the decomposing forces which appear to preside in organic changes. These forces, so far as we can judge, are chiefly of the catalytic class, the azotised albuminous principles of plants having specially the function of ferments, which react generally upon other principles in the same manner, it may be supposed, as we observe diastase to operate during the germination of seeds in converting their starch into gum and sugar. Nature appears to have produced and placed near each principle its peculiar ferment, to effect the conversion of the former into new substances at the proper season. But the action of ferments is a department of chemistry still in its infancy.

Food of Plants.—With the exception of the provision for the first growth of the young plant which exists in its seed, the food of plants appear to be exclusively inorganic. M. Liebig has ably shown that the *humus* or decayed vegetable matter which exists in soils is not absorbed and assimilated by plants—the extremely sparing solubility of that substance being manifestly incompatible with its absorption in any considerable quantity, while even if humus did enter plants, the presumption is that like a solution of gum or sugar absorbed by the roots, it would pass through the plants unchanged, and be excreted by the leaves. The admitted value of humus in soil appears to depend almost exclusively upon its decomposition by the atmosphere, which is greatly assisted by tillage, and the formation of carbonic acid, which gas dissolved in water is taken up by the spongioles of the roots, and supplies the plant with carbon.

The ultimate constituents of all plants are oxygen and hydrogen, carbon, nitrogen, with a small portion of mineral acids and bases in the form of salts; and the condition in which the first mentioned substances enter the plant, adopting the conclusions of M. Liebig, are all the *hydrogen*, and most of the *oxygen*, as water, the *carbon* as carbonic acid, and the nitrogen as *ammonia*. All these matters are derived from the atmosphere.

Water, or its elements in the proportions of water, enters largely into the constitution of vegetable matter, forming 50 per cent of lignin, and an equally large proportion of the other neutral principles, starch, gum, sugar, &c. Certain hydrogenated compounds are also found in plants produced by the fixation of the hydrogen of water without its oxygen, which are employed by the plant for accessory purposes. They form the volatile oils which serve as its defence against the ravages of insects; the fixed oils, or fats, which envelope the seed, and which serve to develope heat by burning at the period of germination; and the wax with which the leaves and fruit are coated to render them impermeable to water.

Carbonic Acid is found as a constituent of air in a proportion varying from 4 to 6 10,000ths. of its volume. Small as this quantity appears it is shown to exceed considerably in amount the whole carbon existing both in living vegetables and in the fossil state as mineral coal. The variation in the proportion of carbonic acid by night and by day, in winter and in summer is rightly judged by M. Dumas to be a simple meteorological phenomenon, depending upon this gas being brought down in rain, and absorbed and retained in largest proportion by water in the cold season. The gas is directly absorbed from the atmosphere by the leaves, and also from the humid soil by the roots of plants. Boussingault observed vine leaves in a glass vessel to absorb completely the carbonic acid from the air as fast as it was carried to them, however rapid the current through the vessel. M. Boucherie has also observed enormous quantities of carbonic acid to escape from the trunk of a tree cut when in full sap, evidently aspired from the soil by the roots. Under the deoxidating influence of light, plants decompose carbonic acid retaining its carbon for their own use, and returning its oxygen to the atmosphere. Their green leaves absorb the chemical rays of the sun so completely, as to give no image in the Daguerreotype. Plants thus possess energetic means of reduction which cannot be imitated, for chemists are ignorant of any method of decomposing carbonic acid in the cold. Plants, however, also exhale carbonic acid, particularly in the absence of light, and this has been supposed analogous to the expiration of carbonic acid by animals, and depending upon the respiration of plants. M. Liebig, however, looks upon this exhalation as entirely physical, as the escape by diffusion into air of the carbonic acid dissolved in the fluids of the plant, in the absence of the reducing light; the carbonic acid being derived by the roots from decomposing humus, and this exhalation most considerable from plants growing in a rich soil. Thus, at night, plants allow the carbonic acid to pass through them, without absorbing it.

Ammomia also finds its way into the atmosphere, being a product of the putrefactive decomposition of all azotised bodies, and is evolved from them principally in the condition of the volatile carbonate. The existence, however, of this substance in the air must be transient, as from its solubility in water, it will be brought down to the earth by every shower. It thus enters the plant by its roots. Another source of ammonia is animal manure, particularly urine, which in a putrid state is rich in salts of ammonia. There can be little doubt that nitrogen, in the form of *nitric acid*, can also be assimilated by plants, as appears by the favourable action of nitrate of soda, nitrate of ammonia, and other nitrates upon vegetation.

According to the observations of M. Boussingault, the Jerusalem artichoke and leguminous plants generally can assimilate the *free nitrogen* of the atmosphere, to a small extent, but the cereals and other plants are entirely destitute of that power.* The quantity of nitric acid or nitrate of ammonia produced in the atmosphere by lightning, must be utterly insignificant, although some importance has been assigned to this as a source of the azotised food of plants.

Of the fixed earthy and saline constituent of plants which are derived from the soil, and are found in their ashes when burnt none is more generally necessary than the *silicate of potash*, which is produced in most soils by the gradual decomposition, under atmospheric influences of the felspathic minerals they contain, or is added in the form of the ashes of burnt wood and plants. *Earthy phosphates* are quite essential to the cereals, and are added to the soil in animal manure; hence the constant remark that the cereals, like the domestic animals naturally follow man in his migrations.

The vegetable kingdom is undoubtedly the great laboratory in which organic substances are produced, for from the substances enumerated, water, carbonic acid and ammonia, and not from any store of original matter in the soil are the principles in plants derived. The steps of the conversion of these into the organic principles in the organism of the plant escape detection, but the general character of vegetable action is of a reducing nature, such as the Sun's light favours, carbonic acid certainly and probably water being decomposed, their carbon and hydrogen retained, and their oxygen returned to the atmosphere.

Food of Animals.—The organic matters produced by plants form the food of animals; for animals produce little or no organic matter, but on the contrary destroy it. Indeed the character of the chemical action of animals is exceedingly well defined, and the reverse of that of plants. The animal frame may be looked upon as an apparatus of combustion, in which the reduced hydrogen and carbon of plants are again oxidated as in a furnace, and returned to the atmosphere in the form of water and carbonic acid. Thus are sustained the animal heat, and the powers of locomotion of animals. While carbonic acid and nitrogen in the form of salts of ammonia are supplied to the vegetable world.

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* Ann. de Chim. et de Phys. t. 76, p. 5 and t. 69, 353.

Animals require azotised food for their growth, for all the great constituents of the animal frame, such as its fibrin albumen, and casein are azotised matters; nothing indeed is found in the soft parts of the body which is not azotised, except water and fat, neither of which is organised. For the renewal of these parts, a constant supply of azotised food is also necessary. Gum, starch, and sugar, which contain no nitrogen, are incapable alone of supporting life for any considerable period, and animals fed exclusively upon the latter substances eventually succumb with all the appearances of death from starvation.

Respiration.—But elementary substances of the amylaceous class although they afford no element to the body, supply carbon to be burned in respiration, consisting as they do of carbon with oxygen and hydrogen in the proportions of water. In the lungs of the higher animals, the dark venous blood is exposed to air through a thin and humid membrane, permeable to oxygen from its solubility; that gas is absorbed by the blood, and imparts to it a fine florid red colour, and the characters of arterial blood. There is no reason to believe that any considerable oxidation occurs in the lungs although the gas is dissolved there by the blood. The latter containing free oxygen is carried by the circulation to the extreme capillaries, where the processes of secretion to which it contributes are most active, and where it will enter into combination in largest quantity. Indeed it has been found by experiment that venous blood absorbs oxygen and becomes red and arterial, without producing the smallest trace of heat.

Carbonic acid being formed is carried by the venous blood to the lungs where it escapes, at the same time that the blood obtains oxygen from the air and is arterialised. From the accurate observations of Professor Magnus on the gases of the blood, it appears that blood gives out from one tenth to one eighth of its bulk of gas when placed in vacuo; that the gas obtained from both arterial and venous blood contains nitrogen, oxygen and carbonic acid; but that while the oxygen in venous blood is at most from one fourth to one fifth of the volume of the carbonic acid, the oxygen in the arterial blood equals at least one third and sometimes almost half of the volume of the carbonic acid in the same blood.* The solvent power of the serum of the blood of the ox, for carbonic acid was found, by M. Scherer, to be double that of pure water; the serum dissolving twice its bulk of carbonic acid, while water dissolves only an equal bulk of that gas, at the usual temperature of the atmosphere.

The air of an easy expiration amounts to 15 or 18 cubic inches, and contains about 3½ per cent of carbonic acid. The air of a deep expiration contains 6 or 8 per cent of that gas, and will not support the combustion of a candle. According to Mr. Coathupe, the quantity of air which passes through the lungs of a man of ordinary size, in twenty-four hours, is 266⅔ cubic feet, of which 20⅔ cubic feet are changed into carbonic acid.† The quantity of carbon thus thrown off daily from the system is considerable, and is found by M. Liebig to be in proportion to the animal heat evolved and exercise taken, and thus varies considerably in different individuals. The proportion of carbon expired by himself is 8½ ounces daily, by a soldier 13½ ounces, by prisoners in close confinement 7 ounces, and by a boy who takes considerable exercise 9 ounces. In an experiment made on a large scale, in which the quantity of carbon in the food and also in the excrements and urine of 856 soldiers was ascertained and compared, it was found that the carbon of the latter amounted only to one twenty-seventh part of the carbon of the former; and consequently twenty-six twenty-sevenths of the whole carbon in the food was converted into carbonic acid and discharged by the lungs.

When the expired air of man and birds is examined, the proportion of oxygen which has disappeared has generally been found sensibly the same as that of the carbonic acid produced; while it will be remembered that oxygen is converted into carbonic acid, by the combustion of carbon, without any change of volume. Such should be the result if the oxygen absorbed in respiration is wholly consumed in oxidating carbon, as it must be when the food is purely farinaceous; such articles of diet as starch, sugar and gum containing already sufficient oxygen to convert their hydrogen into water, and requiring oxygen therefore to burn their carbon only.

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* Annales de Chimie et de Physique, t. 65, p. 182.

† Phil. Mag. 3rd Ser. v. 14. p. 401.

According to some observations, upon which reliance may be placed, the oxygen which disappears in the respiration of man is always a little more than the volume of carbonic acid produced, which would indicate that a part of the oxygen is consumed in oxidating other principles besides carbon, such as the sulphur and phosphorus which are discharged in an oxidated state in the urine; and to a greater extent probably, in oxidating hydrogen, with formation of water. In the respiration of carnivorous animals, the proportion of oxygen which disappears, without being replaced by carbonic acid, is considerable, according to the observations of Dulong, a fact which may be connected with the decided excess of hydrogen over oxygen, in the composition of their food. Carbonic acid is also exhaled from the skin of man and other animals, as well as from the lungs. The question of the absorption of nitrogen from the air, in the respiration of animals, has been finally settled in the negative:, they are incapable of assimilating that element in a free state. (Boussingault: Ann. de Chim. &c., lxxi, 113, and 128). It is certain, however that nitrogen is occasionally exhaled from the lungs, in a sensible quantity, (Edwards,) and must come from the decomposition of an azotised constituent of the blood.

The fat of animals is a provision for the supply of oxidable matter in respiration, and speedily disappears in the absence of food, without a particle of it being discovered in the urine or feces. Fat is most abundant in herbivorous animals, because their supply of food from the vegetable kingdom ceases in winter, and is a provision for their sustenance during that period; on the contrary the bodies of carnivorous animals in a state of nature are entirely destitute of fat. (Liebig.)

The following theory of respiration or of the action of oxygen upon the blood, proposed by MM. Dumas and Boussingault, has a high degree of probability. Under the influence of the oxygen absorbed, the soluble matters in the blood are supposed to be converted into lactic acid, an acid which has been observed in the blood by Mitscherlich, Boutron-Chalard and Fremy. The lactic acid itself becomes lactate of soda, and undergoing a true combustion from combination with oxygen is converted into carbonate of soda. The last salt is decomposed in its turn by a new portion of lactic acid, and the carbonic acid set free, with which the venous blood comes charged to the lungs. The conversion of farinaceous matters into lactic acid, out of the body, by the action of a special ferment, is a fact well understood; and the discharge by the urine, of salts of the organic acids, such as tartrates, acetates and citrates, in the form of alkaline carbonates, has also long been observed. The large production of lactic acid in the blood, and its conversion by oxidation into carbonic acid may therefore be admitted.

The oxidation occurring in respiration is quite sufficient to account for the *animal heat.* MM. Dulong and Depretz observed an excess of heat, in their experiments upon animals, which was ascribed by them, and by physiologists generally, to a calorific power peculiar to the animal and independant of respiration. But in these experiments it was assumed that an animal placed in a calorimeter with cold water, leaves it having exactly the temperature with which it entered; a thing absolutely impossible, as is now known. The cooling of the animal occasioned the excess of heat obtained in their experiments.

The animal frame appears thus to have eminently the character of an apparatus of combustion, by which the complex substances which are formed in the vegetable world and serve as food to animals, are converted again into simpler forms of matter, such as carbonic acid, water and other oxidated products, which are returned to the atmosphere and to the soil to become again the food of plants.*

Digestion.—The principal constituents of flesh and the animal fluids are all azotised substances, namely fibrin, albumen and casein, the last existing in milk and being the basis of cheese. Two very important conclusions have lately been drawn respecting the relations of these substances to each other, and their origin in the vegetable kingdom. The first is a deduction from the analysis of these substances by M. Mulder, which has been repeated and confirmed in the Giessen laboratory, namely, that these three substances are identical in composition. The following are the results of M. Mulder's analyses:

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* "To mount to the summit of Mont-Blanc, a man requires two days of twelve hours. During that time he burns on an average 300 grammes (10 ounces and 258 grains avoirdupois) of carbon or the equivalent of hydrogen. If a steam engine were employed to carry him there, it would burn from 1000 to 1200 grammes, to do the same work."—*Leçon sur la Statique chimique des êtres organisés, professée par M. Dumas.*

	FIBRIN.	ALBUMEN.		CASEIN.
		Of eggs.	Of serum.	
Carbon . .	54.56	54.48	54.84	54.96
Nitrogen . .	15.72	15.70	15.83	15.80
Hydrogen .	6.90	7.01	7.09	7.15
Oxygen Phosphorus Sulphur	22.82	22.81	22.24	22.09
	100.	100.	100.	100.

The proportion of the carbon to the nitrogen in these substances is that of 8 equivalents of the former to 1 of the latter. They differ slightly in the minute quantity of phosphorus and sulphur with which they are accompanied. They all dissolve in concentrated hydrochloric acid, with the aid of heat, and the solutions kept for a time at a pretty high temperature, first assume a beautiful lilac, and then a rich violet blue colour. At this stage of the decomposition, each of the three substances re-acts in the same way with carbonate of ammonia and other re-agents. With considerably different physical properties, they appear to be modifications of a common principle, which Mulder names Protein, and expresses by $C_{40}H_{31}N_5O_{12}$; Liebig, by $C_{48}H_{36}N_6O_{14}$.

The second conclusion is the observation of M. Liebig, that animals draw these principles ready formed from the vegetable kingdom, and do not organise them. The parallel vegetable principles are vegetable fibrin, a constituent of gluten first properly distinguished by Liebig, and gluten itself, vegetable albumen, and legumin, or as it is termed by Liebig, vegetable casein; the latter two being identical, equally in properties as in composition, with animal albumen and animal casein. This appears by the following analyses which were executed at Giessen.*

VEGETABLE FIBRIN.

	I. (Dr. H. Bence Jones.)	II. (Dr. Scherer.)	III. (Dr. Scherer.)
Carbon . .	53.83	54.603	54.603
Nitrogen . .	15.59	15.810	15.810
Hydrogen .	7.02	7.302	7.491
Oxygen Sulphur Phosphorus	23.56	22.285	22.096
	100.	100.	100.

VEGETABLE ALBUMEN.

	From rye. (Dr. Jones).	From wheat.	From gluten of plants.
Carbon . .	54.74	55.01	54.85
Nitrogen . .	15.85	15.92	15.88
Hydrogen .	7.77	7.23	6.98
Oxygen Sulphur Phosphorus	21.64	21.84	22.39
	100.	100.	100.

	LEGUMIN OR VEGETABLE CASEIN. (Dr. Scherer.)	GLUTEN. (Dr. Jones.)
Carbon	54.138	55.22
Nitrogen	15.672	15.98
Hydrogen . . .	7.156	7.42
Oxygen Sulphur . . .	23.034	21.38
	100.	100.

The vegetable and corresponding animal principles are also accompanied by the same inorganic substances, in small quantity, namely magnesia, phosphoric acid, lime, iron, alkalies and sulphur. They evolve the same fœtid odour when heated, and give the same volatile products containing sulphur and phosphorus.

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* Annalen der Chimie und Pharmacie, xxxix, 129.

Animals thus obtain the constituents of their bodies from plants, if herbivorous, or from the bodies of other animals, if carnivorous, and merely assimilate organic principles without organising them. For the azotised vegetable principles take a new form in the animal organism, without any change in their chemical composition. The albumen, fibrin and casein of the animal system also admit, from the identity of their ultimate composition, of being readily converted one into the other, according as each is required in the animal economy. Animal digestion comes thus to be deprived of much of its mystery. M. Dumas has thus expressed himself, very lately, respecting that process.

" Digestion is a simple function of absorption. The soluble matters pass into the blood, for the most part unaltered; the insoluble matters arrive in the chyle sufficiently divided to be aspired by the orifices of the chyliferous vessels. Digestion has evidently for an object to restore to the blood, a matter proper to furnish for our respiration the ten or fifteen grammes of carbon or the equivalent of hydrogen, which every individual burns per hour, and also to provide the gramme of nitrogen, which is exhaled every hour, in part by the lungs and skin, as well as by the urine. Thus, amylaceous matters are converted into gum and sugar; the saccharine matters formed are absorbed. The fat matters are divided, form an emulsion, and so pass into the vessels, to form afterwards deposits, which the blood takes up and burns, when they are required. The neutral azotised matters, the fibrin, albumen and casein, first dissolved, then precipitated, pass into the chyle highly divided or dissolved anew.

" An animal, therefore, receives and assimilates almost untouched, the neutral azotised matters which he finds ready formed in the animals or plants upon which he lives; he receives oily substances which come from the same sources, and also amylaceous and saccharine substances of the same origin. These three orders of matters, of which the origin is always traceable to the plant, divide themselves into products admitting of assimilation; into fibrin, albumen, casein, and oily bodies, which serve to increase or renew the organs; and into combustible products, sugar and the oily bodies, which are consumed in respiration. An animal thus assimilates, or destroys ready formed organic matters; it creates nothing."

Although the usual function of plants is to act, under the influence of the solar rays, like apparatus of reduction, in which water, carbonic acid and ammonia are decomposed, yet in some circumstances, they act differently and more like animals. In the germination of the seed, much heat is produced, with the formation of carbonic acid and water. The starch of grain in malting is observed to pass first into gum, then into sugar, and lastly to disappear, producing carbonic acid. Sugar thus seems to be the agent, by means of which plants as well as animals develope the heat they require. The fecundation of plants is always accompanied by heat, the flowers respiring and producing carbonic acid. They must, therefore, consume carbon; and accordingly we find that the sugar in the stems of the sugar-cane has entirely disappeared after the flowering and fructification are completed. The shot beet, turnip and carrot contain no longer a trace of sugar in their roots. The oils accumulated in some seeds appear to serve, like the fat of animals, to support this respiration, and to supply the heat, by their combustion, which plants require at certain periods of their growth, and for the discharge of certain functions.

The curious observation has also been made by M. Morren, that certain green animalculæ found in stagnant water, perform the usual function of the green parts of vegetables, decomposing carbonic acid and evolving oxygen, under the influence of the light of the sun. The proportion of free oxygen in the water is frequently raised, by their action from 30 to 56, or 57, or even to 61 per cent, while carbonic acid disappears in a corresponding proportion. It is in the *enchelide monad*, (of Bory,) only, and some other green animalculæ higher in the series, that this phenomenon is observed.*

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*Ann. de Chim. et de Phys. 3 ser. 1. 456.

SECTION II.

MODIFICATIONS OF PROTEIN: ALBUMEN, FIBRIN, CASEIN.

ALBUMEN.

This substance forms the white of eggs, whence its name, and is the principal constituent of blood; it is also found in many fluid secretions, and in nearly all the solids of the animal body. It exists in two conditions, soluble, as it is in the animal fluids, and insoluble or coagulated, when heated to 158°.

Uncoagulated albumen may be prepared by evaporating the clear serum of blood, or white of egg, by a heat of 120°, till it dries up and forms a yellowish transparent brittle mass, like gum. This is reduced to powder, and washed successively with ether and alcohol, which dissolve out the fat, salts and other foreign matters in the serum or white of egg.

Dry albumen first swells up in water, then forms with it a glairy colourless fluid, which is nearly tasteless. At 140° the dry albumen begins to lose its transparency, and at 142° it changes into a white coherent mass, in which the albumen has passed into the insoluble condition. When dissolved in water it coagulates at 158°; a very dilute solution, however does not become turbid till it is boiled. Albumen is thrown down from solution, in a coagulated state, by alcohol, creosote, by acids particularly nitric acid; by metaphosphoric acid, but not by the other hydrates of phosphoric acid, nor by acetic acid. The precipitates with acids are definite compounds of albumen with the latter. Coagulated albumen also forms compounds with acids, which are insoluble in an excess of the acid, but are soluble in water. Dilute hydrochloric acid precipitates albumen, the concentrated acid when heated dissolves the coagulum, of a lilac and then of a deep blue colour, as it also dissolves fibrin and casein. Albumen is precipitated from its soluble compounds with acids, by the ferrocyanide of potassium. Coagulated albumen dissolves in caustic alkalies and neutralises them; the solutions are precipitated by soluble metallic salts, and insoluble albuminates of the metals formed.

A solution of albumen in water is precipitated by acetate of lead, and many other metallic solutions. Insoluble compounds are formed, one of which is of considerable interest, that of chloride of mercury; as albumen is had recourse to as an antidote to corrosive sublimate, the white of one egg precipitating about four grains of that salt. To form the *albuminate of chloride of mercury,* a solution of corrosive sublimate is added in excess to a solution of albumen, and the white flaky precipitate is collected on a filter and washed. It is slightly soluble in water, resembles the curd of milk and is insipid; it dissolves in a solution of common salt. Lassaigne finds that when heated it coagulates; the albumen appearing to abandon chloride of mercury, at the same time, which may afterwards be dissolved out by ether. It consists, when dried, according to the same chemist, of 93.4 parts of albumen and 6.6 parts of chloride of mercury, in 100 parts. Chloride of mercury forms a similar compound with fresh fibrin. The solution of albumen is also precipitated by an infusion of nutgalls.

Soluble albumen dissolves phosphate of lime, a salt, of which about 2 per cent may be separated from coagulated albumen by dilute hydrochloric acid. Metallic silver is blackened by albumen, which always contains sulphur, whether the albumen is soluble as in the egg and blood, or insoluble as in the hair.

FIBRIN.

This principle is contained by the living blood in a soluble state, but soon coagulates when withdrawn from the blood vessels. It forms the clot of coagulated blood, and constitutes muscular fibre. It is obtained in threads on stirring newly drawn blood with a stick; or by pressing the coagulum in a small stream of water, till it becomes colourless and consists of soft fibres. It is purified by washing it with ether, or warm anhydrous alcohol which dissolves out fat.

Fibrin affects a remarkable kind of aggregation, the globules of which it is composed, attaching themselves to each other by their ends, so as to form threads or fibres. In the humid state it possesses the characteristic softness and elasticity of the flesh of animals, and contains about three-fourths of its weight of water. It may be deprived of this water in dry air, and then becomes a hard and brittle substance; but, like flesh, it imbibes water again when moistened, and recovers its original softness and elasticity. It always leaves, like albumen, when burned, a portion of phosphate of lime.

Fibrin is insoluble in alcohol, ether and water. When boiled for a long time in water, particularly under pressure, its nature is altered and it becomes soluble. Coagulated albumen comports itself in the same way. Fibrin forms compounds with both acids and bases. In concentrated acetic acid it swells up and forms a transparent colourless jelly, which dissolves in a considerable quantity of boiling water. This solution is precipitated by ferrocyanide of potassium. In other concentrated acids fibrin undergoes a similar change. Fibrin dissolves in caustic alkalies and neutralises them. It is separated from them by acids, and precipitated.

The fibrin of venous blood may be entirely dissolved in a solution of nitrate of potash, although not without rubbing in a mortar and digestion in the cold for some time. The solution is coagulated by heat, and greatly resembles a solution of albumen, (Berzelius, Scherer). This solubility in nitre is not possessed by fibrin from the following sources: arterial blood, the "buffy coat," and that obtained by stirring blood, nor by fibrin after exposure for some time to the air, or fibrin boiled in water for a few minutes, or digested in alcohol. M. Scherer observes that, when in the soluble condition, fibrin is a highly alterable substance, absorbing oxygen readily and emitting carbonic acid; but after being boiled for a few minutes it produces no carbonic acid in an atmosphere of oxygen gas. He concludes that fibrin, although always insoluble in pure water, has still an uncoagulated and coagulated condition, like albumen; that it is uncoagulated in the clot of venous blood, and when soluble in a solution of nitre; but coagulated as it exists in arterial blood, from the absorption, he supposes, of oxygen, and after being boiled for a few minutes, or treated with alcohol. The decomposition of peroxide of hydrogen, with evolution of oxygen gas is occasioned, he finds, by fresh fibrin from all kinds of blood, but not by boiled fibrin; nor is the decomposition produced, it will be remembered, by coagulated albumen. A solution of venous fibrin in nitre, contained in a deep cylindrical jar, allows a precipitate in fine flocks to fall, when the jar is open, but not when it is covered and access of air prevented. This precipitate is insoluble in the solution of nitre, and possesses the properties of arterial fibrin.*

PROTEIN.

Formula: $C_{40}H_{31}N_5O_{12}=Pr$ (Mulder). When albumen or fibrin is dissolved in a moderately strong solution of caustic potash, and heated to about 120°, the small portions of phosphorus and sulphur which it contains, are separated in the form of phosphate of potash and sulphuret of potassium; and when this solution is saturated with acetic acid, a gelatinous substance precipitates which is the same from both fibrin and albumen, and constitutes protein. After being washed, protein is still gelatinous, of a greyish colour, and semi-transparent. When dried it is yellowish, hard, easily pulverised, tasteless, insoluble in water and alcohol. Like albumen and fibrin it is not fusible by heat witbout decomposition.

Albumen and fibrin may be considered as compounds of protein with sulphur and phosphorus in different proportions. Mulder found in fibrin and in the albumen of eggs from 0.36 to 0.38 per cent of free sulphur, with from 0.32 to 0.43 per cent of free phosphorus, which quantities of these elements are in the proportion of $SP\frac{1}{2}$. In albumen from the serum of blood, 0.68 per cent of sulphur, and 0.33 per cent of phosphorus were found, or $S_2P\frac{1}{2}$. The composition of these substances is thus represented by Mulder:

Fibrin, and the albumen of eggs . . .	$10\ Pr+S\ P\frac{1}{2}$
Albumen of serum	$10\ Pr+S_2P\frac{1}{2}$

The oxides of lead and silver likewise combine with 10 atoms of protein. The globulin of blood, vegetable albumen, and the casein of milk, treated with alkalies, in the same way as fibrin and albumen, give also a protein which is identical in composition and properties with the foregoing.

M. Liebig has adopted for protein the formula $C_{48}H_{36}N_6O_{14}$, which is different from that of Mulder, although equally compatible with the analytical results. It gives the composition of protein, per cent.

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* Scherer, *chemisch-physiologische Untersuchungen*. Annalen der Chemie, &c., X., October), (1841).

Carbon	55.742
Hydrogen	6.827
Nitrogen	16.143
Oxygen	21.288
	100.000.

M. Dumas represents the composition of protein differently, I am not aware upon what authority, assigning to it more oxygen, than Mulder and Liebig. His formula is $C_{48}H_{35}N_6O_{17}$; which is 48 atoms of carbon with the elements of 6 atoms of ammonia and of 17 atoms of water. The combustion of protein and all its compounds is effected with difficulty in the combustion tube; to burn the carbon completely, M. Scherer found it quite necessary to mix chlorate of potash with the oxide of copper, or to burn with chromate of lead.

Protein combines with both acids and bases, and is soluble in all acids when highly diluted. In combining with acids it forms new compound acids; with sulphuric acid *sulpho-proteic acid*, $Pr+SO_3$. It combines also with 2HCl. *Chloroproteic acid*, $Pr+ClO_3$, is formed on passing chlorine gas through a solution of albumen, and precipitates in white flocks. The same compound is formed by the action of chlorine on ammoniacal solutions of casein and fibrin (Mulder).

Xanthoproteic acid, $2HO+C_{34}H_{24}N_4O_{12}$ (Mulder), is formed when albumen, or any other protein-compound is digested in nitric acid. The albumen, &c., dissolve of a yellow colour, with escape of nitrogen gas, and the formation of oxalic acid and ammonia. Two atoms of protein, 1 of water, and 2 of nitric acid, yielding 3 of oxalic acid, 2 of ammonia and 1 of hydrated xanthoproteic acid as represented above. After being washed with boiling water, this acid forms a tasteless orange-yellow powder, which combines equally well with acids as with bases. The salts containing the last dissolve in water of a dark red colour.

Leucin, $C_{12}H_{12}NO_4$, a substance discovered by Braconnot. When boiled with caustic alkali in excess, protein or any protein-compound is completely decomposed, and ammonia, carbonic acid, formic acid, and three azotised bodies, are formed: leucin, protid and erythroprotid. The alkaline solution is neutralised with sulphuric acid, poured off from the sulphate of potash which precipitates, evaporated to dryness, and the mass boiled with alcohol. *Erythroprotid*, is first deposited, as a reddish brown extractiform mass. This substance, as it exists in combination with oxide of lead, is expressed by $C_{13}H_8NO_5$, Later, the leucin separates in a crystalline state. *Protid*, $C_{13}H_9NO_4$, which is a yellowish uncrystallizable brittle substance, remains in solution, with formiate of potash. The leucin crystallizes in brilliant plates, like cholesterin, is inodorous and tasteless, and sublimes unchanged at 338°. It is but slightly soluble in water, and still less soluble in alcohol. It is not decomposed by alkalies. It combines with 1 atom of the protohydrate of nitric acid, and becomes *nitroleucic acid*, which forms crystalline salts containing 1 atom of base, without losing its leucin. The same substance is also formed by the digestion of a protein-compound in sulphuric acid.

CASEIN.

The curd or coagulable portion of milk has been named casein and also *caseum*; it is a principle having considerable analogy to albumen, coagulable by rennet but not by a boiling temperature. Sweet milk contains its whole casein in solution, with globules of fat in a state of suspension, which last rise to the surface in the form of cream, or are separated, by agitation of the milk, in the form of butter. The milk contains also in solution a considerable quantity of lactine or sugar of milk (page 755), to which the casein stands in the relation of a ferment. The latter soon begins, probably after being affected like other ferments by the air, to convert the lactine into lactic acid (page 809). Milk thus spontaneously becomes sour in open vessels, and its casein is at the same time coagulated by combining with lactic acid (Fremy).

Casein combines with other acids, besides the lactic, and is best prepared according to Braconnot, by adding dilute sulphuric acid to skimmed milk; a white coagulum is formed, the sulphate of casein insoluble in water, which may be collected and washed upon a filter. It is afterwards digested with carbonate of lead, which abstracts the sulphuric acid, and the casein becoming free is dissolved by the water. The solution of casein is evaporated to dryness, the dry matter reduced to powder and digested in boiling ether, to dissolve out fat; the residue of casein is afterwards dissolved again in water, and precipitated by the addition of alcohol, to separate it from other matters.

When dry, casein is yellowish like gum, insipid, and does not dissolve again readily in water. Its solution is also yellowish and somewhat viscid, and smells like boiled milk; left to itself it putrifies and smells like old cheese. It comports itself with reagents very like albumen; it is precipitated by acids, even by acetic acid which does not affect albumen. The precipitates formed are soluble in an excess of their acid, and also, it is said, in alcohol. Like albumen, casein exists both in a liquid and solid form. Its coagulation is effected by *rennet*, the inner coat of the calf's stomach, after it is well washed in hot water. Skimmed milk placed in contact with a small portion of this membrane, or mixed with an infusion of it, and heated to 90° or 100°, is thickened, and coagulates so completely that not a trace of the casein remains dissolved in the whey. This action of rennet is that of the pepsin it contains, but how the latter operates is unknown. Berzelius observed that 1 part of the membrane, washed and dried, placed in 1800 parts of skimmed milk gradually heated up to 122°, occasioned complete coagulation. The membrane taken out afterwards, washed and dried, was found to have lost 6 per cent of its weight. The coagulum, mixed with the fat or butter, in sweet milk, strongly compressed and dried, forms *cheese*. The fat may be dissolved out of the latter by ether.

Coagulated casein is insoluble or only very sparingly soluble in water. It dissolves easily in dilute warm vinegar and alkalies. Casein always leaves behind it, on incineration, a portion of phosphate of lime, which milk contains in considerable quantity. Casein contains a little sulphur but no phosphorus, in chemical combination. It belongs to the class of protein compounds, and may be considered a combination of 10 atoms of protein with 1 atom of sulphur. Its identity with vegetable legumin (page 912) has already been more than once adverted to.

When milk is heated in an open vessel, it soon becomes covered by a pellicle composed of insoluble matter. M. Scherer finds that the pellicle is formed by the absorption of oxygen, and does not appear upon milk heated in an atmosphere of carbonic acid.

Fresh and pure blood-serum, mixed with twice its weight of distilled water, and a small quantity of a solution of caustic alkali, soon loses all alkaline reaction, and on heating to the boiling point, the coagulation of the albumen no longer occurs; but the solution when heated becomes covered by a pellicle, like milk. M. Scherer considers this as the conversion of albumen into casein, the pellicle agreeing closely in composition and properties with the pellicle from heated milk.

M. Scherer also finds soluble casein, always to leave, when burnt, a highly alkaline ash containing much lime, but in the coagulated state to leave a neutral ash. The solubility of the casein he, therefore, ascribes to its combination with an alkali, and its coagulation to the saturation of that alkali. The acid which saturates the alkali appears to be the lactic, produced by the change of the sugar of milk, under exposure to air, when the milk is heated.

SECTION III.

PEPSIN, GLOBULIN, HEMATOSIN, GELATIN, CHONDRIN.

PEPSIN.

This is a peculiar animal principle secreted by the stomach and present in the gastric juice. It is usually prepared by infusing the mucous membrane of the fourth stomach of the calf, which is known as rennet, and as obtained from this source is distinguished by the power which it possesses to coagulate milk. This property the infusion loses when boiled, indicating a relation between pepsin and albumen. The infusion, aided with a few drops of hydrochloric acid, and kept at 80 or 90°, dissolves completely portions of albumen boiled hard, of fibrin or boiled meat, in the course of from 12 to 24 hours. By means of this agent the process of animal digestion has been imitated perfectly, out of the body, by Eberle, Schwann and other physiological inquirers.

The most precise information we possess respecting the nature and production of pepsin has been obtained by M.

Wasmann, who first succeeded in isolating it; his observations were made upon the mucous membrane of the stomach of the pig, which greatly resembles that of man.* The organ which secretes the gastric juice consists of glands of a particular nature contained in the mucous membrane of a portion of the stomach. When this membrane is digested in a large quantity of water at from 86° to 95°, without being cut into pieces, but after being well washed, water extracts from it a variety of matters besides pepsin; but if this water be removed and fresh water added and the digestion continued in the cold, nothing almost dissolves now except pepsin. The operation may be continued with new portions of water till the membrane enters into putrefaction; water extracts pepsin at every repetition till at last nothing remains but a tissue, from which hydrochloric acid takes up no matter capable of dissolving hard-boiled albumen.

The solution of pepsin, thus obtained from the glandular membrane, is colourless, somewhat viscid, and is capable, if rendered acid by hydrochloric acid, of dissolving solid albumen very rapidly. It contains besides pepsin a little albumen, which can be separated from the acid solution by ferrocyanide of potassium, a salt which does not precipitate pepsin, or by heating the solution, if not very dilute, to 170°, or to 212° without boiling; the coagulated albumen is then deposited in flocks, with a little modified casein. The filtered liquid is no longer viscid, but preserves the property of dissolving solid albumen with the aid of a little hydrochloric acid. When boiled it becomes turbid again, and loses entirely the power to dissolve the albumen. For when the coagulated flocks are dissolved in acetic acid, they exert no solvent action on hard white of egg, even with the concurrence of hydrochloric acid; the solution of coagulated pepsin in acetic acid is not precipitated by ferrocyanide of potassium.

Pepsin thus appears to be a substance sparingly soluble in water. When its solution is evaporated to dryness, there remains a brown, greyish, viscid mass with the odour of glue and having the appearance of an extract. The solution of the latter in water is turbid, and still possesses a portion of the characteristic power of pepsin, but greatly reduced. On adding to a fresh solution of pepsin 1 or 2 volumes of strong alcohol, the pepsin is precipitated in white flocks which may be collected on a filter. The alcoholic liquid filtered, gives on evaporation a brown deliquescent residue, which reddens litmus and is entirely deprived of digestive powers.

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* Pharmac. centr. Blatt. 1839. p. 349, 353.

The precipitate of pepsin forms white flocks, which, upon drying on the filter, produce a grey compact mass. When moistened with water, it swells up and dissolves in a large quantity of water. It dissolves more easily in water acidulated with acetic or any other acid; this solution is not disturbed by ferrocyanide of potassium, and possesses in a high degree the power of dissolving coagulated albumen. A solution of dried pepsin in pure water is rendered turbid by ebullition, and loses its solvent power for aliments.

Many metallic salts precipitate pepsin, although not entirely, from a fresh solution of the membrane; such as protosulphate of iron, sulphate of copper, acetate of lead, chloride of mercury and protochloride of tin. Pepsin may again be separated from these precipitates by exposing them suspended in water to a stream of sulphuretted hydrogen; but a portion of the acid of the metallic salt remains in combination with the pepsin, forming a compound which has a well marked acid re-action on litmus, and possesses the solvent powers of pepsin in a high degree.

Acetate of pepsin may be obtained by decomposing the precipitate obtained with acetate of lead, by means of sulphuretted hydrogen, then evaporating the solution of pepsin with caution to a syrupy consistence, and treating it with alcohol. The acetate of pepsin remains undissolved by the alcohol, in the form of white flocks, which become a mass, on drying in the air, resembling gum. It does not attract humidity, but dissolves easily in water, with an acid reaction. A solution of the dried acetate in 60,000 times its weight of water, to which a little hydrochloric acid is added, dissolves white of egg in the course of six or eight hours. Alkalies appear to destroy the specific solvent power of pepsin.

Hydrochlorate of pepsin is obtained on precipitating the infusion of the mucous membrane by chloride of mercury, decomposing the precipitate, after being well washed, by sulphuretted hydrogen, and mixing the filtered liquid which contains the pepsin with alcohol, by which the hydrochlorate of pepsin is left undissolved, like the acetate of pepsin. It possesses properties analagous to those of the acetate, and its solution in water dissolves coàgulated albumen very rapidly. The alcoholic liquor above possesses no solvent power; when evaporated to dryness it leaves a residue which resembles an extract of meat.

In regard to the solvent power of pepsin for coagulated albumen, it was observed by M. Wasmann that a liquid which contains 1.7 thousand parts of acetate of pepsin and 6 drops of hydrochloric acid per ounce, possesses a very sensible solvent power, so that it will dissolve a thin slice of coagulated albumen in the course of 6 or 8 hours' digestion. With 12 drops of hydrochloric acid per ounce the white of egg is dissolved in 2 hours. A liquid which contains ½ grain of acetate of pepsin and to which hydrochloric acid and white of egg are alternately added, so long as the latter dissolves, is capable of dissolving 210 grains of coagulated white of egg at a temperature between 95° and 104° It would appear, from such experiments, that the hydrochloric acid is the true solvent, and that the action of the pepsin is limited to that of disposing the white of egg to dissolve in hydrochloric acid. The acid when alone dissolves white of egg, by ebullition, as it does under the influence of pepsin; from which it follows that pepsin replaces the effect of a high temperature which is not possible in the stomach. The same acid with pepsin dissolved blood, fibrin, meat and cheese, while the isolated acid dissolved only an insignificant quantity, at the same temperature; but when raised to the boiling point it dissolved nearly as much, and the part dissolved appeared to be of the same nature. The epidermis, horn, the elastic tissue (such as the fibrous membrane of the arteries) do not dissolve in a dilute acid containing pepsin.

M. Wasmann has remarked that the pepsin of the stomach of the pig is entirely destitute of the power to coagulate milk, although the pepsin of the stomach of the calf possesses it in a very high degree, from which he is led to suppose that the power of the latter depends upon a particular modification of pepsin, or perhaps upon another substance accompanying it, which ceases to be formed when the young animal ceases to be nourished by the milk of its mother.

HEMATOSIN.

The blood so long as it flows in the veins consists of a clear liquid with floating globules observed by the microscope, which in the higher mammiferous animals are lenticular and circular or elliptical in form, of an orange red colour, and marked with a colourless spot in the centre, or nucleus. From these globules Berzelius derives two of the most characteristic constituents of the blood hematosin and globulin, which are both closely related to albumen. The clear liquor of the living blood, on the other hand, is composed of two principles already considered, namely fibrin and albumen.

To prepare, hematosin blood which has been freed from fibrin by stiring it well, is mixed with 6 times its bulk of a saturated solution of sulphate of soda, in which the blood globules are insoluble, and the latter collected on a filter. The dark-red gelatinous mass is boiled with alcohol, to which a little sulphuric acid has been added. The hematosin is thereby dissolved, while the globulin remains in combination with sulphuric acid, as a colourless or grey mass. The alcoholic solution while yet hot is mixed with carbonate of ammonia, and filtered from sulphate of ammonia and some globulin which precipitate. The solution is reduced to about 1-12th by distillation, whereby the hematosin remains as an insoluble pulverulent residue.

Hematosin is of a dark-brown colour, tasteless and insoluble in water, alcohol, and ether. It dissolves of a red colour in alcohol containing either an alkali or an acid. In aqueous solutions of the alkalies it dissolves of a dark blood-red colour; it is insoluble in hydrochloric acid. When burned it leaves behind a notable quantity of peroxide of iron. The analysis of hematosin gives:

		Atoms.
Carbon	65.84	44
Hydrogen	5.37	22
Nitrogen	10.40	3
Oxygen	11.75	6
Peroxide of iron	6.64	1
	100,00	

M. Scherer has, however, shewn that the oxide of iron is not essential to hematosin, nor necessary to the colour of blood. The matter of the blood globules after being dried was intimately mixed in a mortar with concentrated sulphuric acid, and the mass afterwards diluted with distilled water, and allowed to settle. The liquid above was perfectly clear and colourless, and contained sulphate of iron. The insoluble blood-mass was washed on a filter with water, so long as the washings contained iron. Boiled afterwards in alcohol, the mass coloured the spirit intensely red. On neutralising the sulphate of the colouring matter, the compound in solution, with ammonia, much albumen fell, which was dried and ignited; it left a white ash, in which not a trace of iron could be detected. The blood red solution in alcohol therefore contained no iron.

GLOBULIN.

This substance is the principal constituent of the blood globules; it is a protein compound and closely allied to albumen. But it has not been isolated, and little is known respecting it. The sulphate of globulin which remains behind in the preparation of hematosin, described above, consists of 4 atoms of protein, united with 1 atom of sulphuric acid. The nature of the matter forming the clear nucleus of the globules is still less understood, but it appears more like coagulated fibrin than anything else.

The matter of the blood globules, or the globulin and hematosin together, may be obtained by mixing blood freed from fibrin, with a solution of sulphate of soda, in which the matter of the globules is insoluble and precipitates; or by draining the serum out of the clot of blood cut into thin slices, upon folds of blotting paper, and afterwards mixing the clot with water, in which the matter of the blood globules dissolves of a brown-red colour and transparent. It is soluble in pure water, insoluble in serum. When its solution is mixed with salts of an alkaline base or with sugar, and exposed to air, it becomes of a lively red. The solution of the matter of the blood globules may be evaporated at 122° without losing its solubility; but when heated it coagulates, before its temperature rises to 181°, and precipitates insoluble. Both in its coagulated and soluble state the matter of the blood globules exhibits similar effects with reagents as albumen in the same conditions. M. Simon has lately maintained that this matter is composed of casein and hematosin, but coagulation by heat is not a property of casein.

GELATIN.

This is the basis of glue, size, and animal jelly, and is obtained by the action of boiling water upon skin, tendons, ligaments, cellular tissue, and serous membranes. These materials are dissolved almost entirely, by continued digestion in boiling water, and the solution forms a jelly on cooling. A substance is obtained from the permanent cartilages, by a similar treatment, which also gelatinizes, but is not precipitated by tannin, and differs in other respects from gelatin; the latter substance was first distinguished, as a peculiar principle, by Müller, and named chondrin. Gelatin is not found in the blood or any of the healthy fluids, nor does it exist as such in the solids, but is a product of their alteration by boiling water, as dextrin and starch-sugar are products of the alteration of starch by the same agent.

Gelatin is distinguished by its ready solubility in warm water, and property of forming a stiff jelly when it cools. As prepared from different materials, gelatin differs considerably in viscidity. Its viscidity, as prepared from skins, is inversely as their softness and flexibility. The most adhesive of its forms, *glue*, is prepared from the clippings of hides, hoofs and other refuse of the tan-yard. The solution is boiled, filtered above 120°, and after evaporation poured into square boxes to gelatinize. The jelly is cut into slices, and when dried in the air upon a netting takes the form of the cakes of glue. Glue is dissolved for use by a water-bath heat, after being softened by steeping in cold water. *Size*, which is less tenacious and adhesive, is prepared from parchment, fish skin and several animal membranes; *isinglass* from the entrails of several species of fish, particularly the sturgeon. The latter gelatin gives a colourless solution, which has no disagreeable taste or odour; it forms a firm jelly on cooling when dissolved in 100 times its weight of water.

Gelatin is insoluble in alcohol and ether. When burned it leaves behind a small portion of bone-earth. Its solution in water is not precipitated by alum, by neutral protosulphate of iron, by either the neutral or basic acetate of lead; all of which precipitate a solution of the chondrin of cartilage. Gelatin is readily soluble in diluted acids and alkalies. Its solution in acetic acid is very gluey, but does not gelatinize. Gelatin is not precipitated by corrosive sublimate, which throws down albumen.

Gelatin forms a white compound with tannic acid, *tanno-gelatin*, which is precipitated by a strong infusion of gall-nuts, from a solution of gelatin in 5000 times its weight of water. The white flocks adhere to each on stirring, aud form a soft, tenacious, and elastic mass, which is of the same composition with, and has considerable resemblance to leather. The skins of animals are tanned, after being cleaned and deprived of the cuticle and hair by lime-water, and allowed to enter into a degree of putrefaction to soften them, by submitting them to the action of infusion of oak bark, or other astringent vegetable matter, the strength of which is gradually increased until a complete combination takes place. The tannin is taken up by the skin, of which the weight is considerably increased by this treatment. In the tanning of thick sole-leather many months' digestion in the tan-pit is required, but the process has of late been considerably shortened by slightly heating the infusion of oak-bark by means of steam. The skin is greatly altered by its combination with tannic acid, losing its solubility in boiling water, and becoming nearly indestructible by atmospheric agencies; the animal matter it contains is no longer suitable for the preparation of prussiate of potash, by fusion with an alkali.

" *Tawed leather* is made by impregnating the skin duly prepared by washing in potash liquor, with a solution of alum and common salt; it is afterwards trodden in a mixture of yolk of eggs and water. The alum and salt re-act on each other so as to produce sulphate of soda and chloride of aluminum; the latter salt combines with the skin. White glove leather is thus prepared.

" *Wash leather* is another important manufacture; in this, the skin, after being prepared and softened, is imbued with oil, and afterwards subjected to a weak alkaline solution.

" *Curried leather*, is made by besmearing the skin, or leather, while yet moist, with common oil, which, as the humidity evaporates, penetrates into the pores of the skin, giving it a peculiar suppleness, and making it to a considerable extent waterproof. As familiar examples of these processes, the thick sole leather for shoes and boots is tanned; the upper leather is tanned and curried; the white leather for gloves is tawed; and fine Turkey leather is tawed, and afterwards slightly tanned." (Aikin's chemical Dictionary, art. *Leather*, quoted in Brande's Manual).

Chlorine transmitted through a solution of gelatin throws down a white elastic substance in shreds, which smells of chlorous acid, while humid; it may be obtained in a dry state, by careful drying, and is a definite compound of unaltered gelatin with chlorous acid.

The composition of gelatin has also been examined by M. Scherer. He found isinglass, washed with ether to free it from fatty matters, to leave when burned 0.5 per cent of earthy ashes.

Tendons macerated for a short time in cold water, and afterwards boiled successively in alcohol and ether, and dried at 212°, left on being burned, 1.6 per cent of ashes. The purified tendons, analysed by combustion with chromate of lead, gave:

Carbon.	50.774
Hydrogen.	7.152
Nitrogen.	18.320
Oxygen.	23.754
	100.000

This result was confirmed on repetition of the analysis. It leads to the following empirical formula for gelatin $C_{48}H_{41}N_{15}O_{18}$. M. Scherer observes that if this formula be doubled, gelatin will contain the elements of 2 atoms of protein, with 3 atoms of ammonia, and 7 atoms of oxygen.

Products of the alteration or decomposition of gelatin.—By long digestion, particularly at a temperature considerably above 212°, gelatin loses its power of gelatinizing, and when dried by evaporation forms a yellowish gummy mass, which dissolves easily in cold water.

Concentrated *sulphuric acid* dissolves gelatin, colourless. If the solution is diluted with water and boiled for a long time, gelatin sugar is obtained from it, on saturating with chalk.

A concentrated solution of *caustic alkali* when boiled with gelatin separates ammonia from it, and converts it into leucin (page 1027.) and gelatin sugar. To separate these substances, the alkaline solution is saturated with sulphuric acid, after ammonia ceases to escape, evaporated to dryness, and the mass boiled with alcohol which dissolves out the leucin and gelatin-sugar. The alcohol being distilled off, the residue is washed with small quantities of cold alcohol at a time, by which the very soluble leucin is taken up. The residuary gelatin-sugar may then be dissolved in a larger quantity of boiling alcohol, and crystallizes by spontaneous evaporation.

Gelatin-sugar or *glycicoll*, $C_8H_7N_2O_5+2HO$, crystallizes in pretty large rhomboidal prisms, is colourless, inodorous, and very sweet. It fuses at 352°, but undergoes decomposition; is soluble in 4½ parts of water, in 900 parts of spirits of wine, and insoluble in ether. The solution is precipitated by no metallic salt, nor by tannic acid. But glycicoll combines with oxide of lead, when digested upon it, and then loses two atoms of water (Mulder).

According to a late analyses by Boussingault, who does not appear, however, to have been aware of Mulder's analyses, the composition of glycicoll is $C_{16}\ H_{18}\ N_4\ O_{14}$; of its compound with oxide of silver, $C_{16}H_{15}N_4O_{11}+4\ Ag\ O$. (Ann. de Chim., &c. 3 ser. p. 257).

Glycicoll dissolves without decomposition, in hot nitric acid; it forms a combination with that acid, $C_8H_7N_2O_5+2NO_5+4HO$, which crystallizes in colourless prisms, and forms double salts with bases. The composition of the double salt of lime, which does not deliquesce in air, is $CaO,\ C_8H_7N_2O_5+2\ (CaO,\ NO_5)$.

CHONDRIN.

This variety of gelatin is derived from the permanent cartilages, such as those of the ribs, joints, wind pipe and nose, and cartilaginous bones before ossification, from the cornea of the eye, and also according to Müller, from bones in a state of caries. Chondrin is slowly dissolved out of these substances by boiling water.

The solution of this substance fixes on cooling, like that of gelatin, and when it becomes dry, by evaporation, has the appearance of solid glue. But it is not precipitated by tannic acid; on the other hand it gives precipitates with acetic acid, alum, acetate of lead and protosulphate of iron, which do not disturb a solution of gelatin. Chondrin leaves behind when burned above 4 per cent of bone earth. It appears also, like the protein compounds, to contain a small portion of sulphur in combination.

M. Scherer analysed this substance in its natural state, before it is altered by boiling, operating upon the rib-cartilage of young calves and the cornea. The cartilage was scraped clean by a knife, then digested in water containing some nitrate of potash in solution, to dissolve out albumen, and afterwards boiled in alcohol and ether for the extraction of fat. Dried at 212o, it left when burned 6.6 per cent of earthy ashes. The results of an analysis of this chondrin and also of that of the cornea were as follows:

	From rib-cartilage.	From the cornea.	By calculation.
Carbon.	50.895	49.522	50.745
Hydrogen.	6.962	7.097	6.904
Nitrogen.	14.908	14.399	14.692
Oxygen.	27.235	28.982	27.659
	100.000	100.000	100.000

From which, M. Scherer deduces the following empyrical formula for chondrin, $C_{48}H_{40}N_6O_{20}$. Chondrin thus contains the elements of one atom of protein, with 4 atoms of water, and 2 atoms of oxygen.

Middle coat of the arteries.—This is a highly elastic membrane, of a yellowish white colour. Purified in the same manner as the rib cartilage, and dried at 212°, it left, when burnt, 1.7 per cent of ashes. Its analysis gave a result considerably different from that of chondrin, namely:

	I.	II.	By calculation.
Carbon.	53.750	53.393	53.91
Hydrogen.	7.079	6.973	6.96
Nitrogen.	15.360	15.360	15.60
Oxygen.	23.811	24.274	23.53
	100.000	100.000	100.000

The matter of the middle coat of arteries is therefore represented by $C_{48}H_{38}N_6O_{16}$; which is equivalent to 1 atom of protein plus 2 atoms of water (Scherer).

Membranous and compact horny matter.—This substance is a product of the organism not subject to reabsorption, and differs in that respect from all the others yet considered.

The *membranous horny matter* constitutes the epidermis, in particular, or outer skin, and also the epithelium in its different modes of formation. The *scaly epithelium* which forms the inner surface of the blood and lymph vessels, the inner surface of many mucous and serous sacs, &c. The *columnar epithelium* which forms the surface of the intestinal canal, as well as the surface of the passages from most glands. The *ciliated epithelium* which forms the surface of the mucous membrane of the organs of respiration, &c.

The *compact horny matter* constitutes hair, horn, nails, claws, &c.

I. M. Scherer's analysis of *membranous horny matter* was made upon the epidermis of the sole of the foot. It was first thoroughly washed with water, then boiled in alcohol and ether. Dried at 212°, and then burnt, it left 1 per cent of earthy ashes. Its composition, by two analyses, was:

	1	2
Carbon.	51.036	50.752
Hydrogen.	6.801	6.761
Nitrogen.	17.225	17.225
Oxygen. Sulphur.	24.938	25.261
	100.000	100.000

II. *Compact horny matter.*—Hair was cut into small pieces, well washed and digested in water, and finally boiled in alcohol and in ether. Hair of the beard, thus treated, and dried at 212°, left 0.72 per cent of ashes, when burned; hair of a blond colour from the head gave 0.3 per cent of ashes, the black hair of a Mexican gave 2 per cent of ashes. The substance of nails after similar preparation, gave 0.5 per cent of ashes, wool 2 per cent. Horn gave 0.7 per cent of ashes. Each of these substances was several times analysed, and the results from all were similar, proving that they contain the same principle. Deducting the ashes, as usual, the results of one analysis of each were:

	Hair.	Horn.	Nail.	Wool.
Carbon. .	50.652	51.540	51.089	50.653
Hydrogen. .	6.769	6.799	6.824	7.029
Nitrogen. .	17.936	17.284	16.901	17.710
Oxygen. . Sulphur. .	24.643	24.397	25.186	24.608
	100.000	100.000	100.000	100.000

M. Scherer constructs the following formula to express the results of these analyses, and to exhibit the relation in composition of this class of substances to protein; compact horny matter, $C_{48}H_{39}N_7O_{17}$. This contains the elements of protein plus, 1 atom of ammonia and 3 atoms of oxygen.

Horn, hair, wool and other horny substances dissolve in the solution of caustic alkali, with disengagement of ammonia, and the formation of some acetic acid. When the alkaline solution is neutralised by acetic acid, effervescence occurs from the escape of sulphuretted hydrogen, and a substance falls, soluble in an excess of acetic acid, which possesses the properties and composition of protein. When the solution is precipitated by successive additions of acetic acid, the last additions give a yellowish white precipitate, which is different from the first.

Analyses of the protein from hair and of the other substance, gave the following results:

	Protein from hair.	Other substance from hair.
Carbon. . .	55.150	53.516
Hydrogen. . .	7.197	7.168
Nitrogen. . .	15.727	14.801
Oxygen. . .	21.926	24.515
	100.000	100.000

From the composition of the latter, it is supposed to be the same as the enveloping membrane of the albumen and inner coat of the lining membrane of the egg.

Feathers.—The material of feathers has hitherto been supposed to be of the same nature as horn, but M. Scherer finds the composition of the former to be different, and to have considerable analogy to the second substance derived from hair and horny bodies, as appears by the following analysis :

	Quills.	By calculation.
Carbon	52.427	52.457
Hydrogen	7.213	6.958
Nitrogen	17.893	17.719
Oxygen	22.467	22.866
	100.000	100.000

The composition is calculated, in the second column, from the formula $C_{48}H_{39}N_7O_{16}$. By which feathers are represented as having 1 atom of oxygen less in their composition than horn.

Pigmentum nigrum of the eye.—This matter, carefully removed by M. Scherer from the choroid by means of a hair pencil, in distilled water, was strained with the water through linen, to separate portions of membrane; the liquid with the black matter in suspension was then evaporated to dryness, and the residue boiled in alcohol and ether to purify it. It contains considerably more carbon than any of the preceding substances, as appears by the following analysis :

	Pigmentum nigrum.
Carbon	58.672
Hydrogen	5.962
Nitrogen	13.768
Oxygen	21.598
	100.000

SECTION IV.

SECRETED FLUIDS SUBSERVIENT TO DIGESTION.

Saliva.—This liquid, which is secreted by the salivary glands, contains mucus and very small transparent globules, visible under microscope. It leaves, when evaporated, about 1 per cent of solid matter, consisting of mucus, several salts of potash, of which chloride of potassium is the most considerable, and a peculiar animal substance, which is named *salivary matter*. The latter is soluble in water, not coagulated by boiling nor precipitated by metallic salts. In the salivary glands and ducts of the horse and ass, concretions are sometimes found, which are principally composed of carbonate and a little phosphate of lime. The saliva of man and the sheep generally contains a trace of sulphocyanide of potassium; the saliva of the sheep contains also so much carbonate of soda as to effervesce with an acid.

Gastric juice.—The principal constituent of this fluid is the peculiar principle, pepsin (page 1030). When collected from the stomach during fasting, it is a transparent fluid, of a saline taste, which is neutral, but during the process of digestion it is distinctly acid from the presence of hydrochloric acid.

Pancreatic juice.—This fluid, secreted in the pancreas, is thrown into the duodenum, or the portion of the small intestines nearest the stomach, where it mixes with the partially digested food or *chyme*, as the latter leaves the stomach. It contains albumen in solution and also a matter like casein; its salts are nearly the same as those of the saliva; it has a distinct acid re-action. The uses of this fluid in digestion are unknown.

BILE AND BILIARY CONCRETIONS.

The bile which is contained in the gall-bladder is conveyed to the duodenum and added to the chyme in digestion. It is a greenish yellow fluid, of a peculiar sickening odour, and taste which is at first sweet, but afterwards bitter and exceedingly nauseous. It contains a great variety of substances, of which the most peculiar, which are all in a state of true solution, are bilin, fellinic acid, cholinic acid and biliverdin, according to the latest examination of this secretion, by Berzelius. Besides the acids mentioned, it contains oily acids combined in common with the others with soda, and several other fatty bodies, together with cholesterin. To which are to be added mucus, an undetermined animal matter, common salt, and the other usual salts of animal fluids. The separation of so many substances is extremely difficult, and the more so that the constituents of bile are remarkably prone to assume new forms under the influence of re-agents.

Bilin, the principal constituent of bile, may be isolated by the following processes. (*a*) The bile of the ox, after the separation of its mucus, is mixed with a little acetic acid, then filtered and precipitated by acetate of lead. The yellow precipitate, consisting of a combination of biliverdin, oleic and margaric acids with oxide of lead, is filtered, and the filtered liquid precipitated by a solution of the basic acetate of lead. The last precipitate, at first white, then yellow and plaster-like, contains fellinic acid in combination with a portion of the bile. Most of the bilin remains undissolved. The lead in the same solution is precipitated by sulphuretted hydrogen, and the solution remaining of bilin is evaporated carefully to dryness. The bilin so procured contains acetate of soda, and is likewise somewhat altered by the action of the free acetic acid during the evaporation. It is in this condition that bilin has been distinguished by the name of *bile-sugar* or *picromel*.

(*b*) Ox-bile is evaporated to perfect dryness on a water-bath, reduced to powder and digested with anhydrous ether, which dissolves out all the fatty bodies not in combination with bases. The mass is then dissolved in alcohol, by which, mucus, common salt, &c. are left undissolved. To the filtered liquid a solution of chloride of barium is added, by small portions at a time, so long as a dark green precipitate is formed. The last contains the biliverdin or colouring principle. The liquid filtered from it is then treated with barytes-water, added gradually, so long as a precipitate falls. The colour of different portions of the precipitate, as they are successively produced, is dark grey, soon becoming green, then brownish yellow, and at last yellow. It contains, besides biliverdin, an orange-coloured matter, not yet investigated, and margaric acid.

The liquid filtered from the last precipitate, after the precipitation of the free barytes it contains by carbonic acid, is evaporated to dryness, and the mass dissolved again in anhydrous alcohol, which leaves common salt and chloride of barium undissolved. Sulphuric acid mixed with an equal bulk of water, and then diluted by alcohol, is added gradually to the alcoholic solution to precipitate the bases it contains, in the form of sulphates. The liquid again filtered is mixed with freshly precipitated carbonate of lead, for the purpose of combining its sulphuric acid and oily acids, and the greater proportion of the alcohol then distilled off. The liquid thus concentrated is filtered from the precipitate of lead salts, freed from lead in solution by sulphuretted hydrogen, filtered and evaporated to dryness in a water-bath. The transparent, yellow, bitter mass which remains, and which was formerly distinguished by Berzelius as *biliary matter*, is composed of bilin and fellinic acid.

The last product is dissolved in water and digested with finely pulverised oxide of lead, by which it forms a plaster-like mixture of fellinate and cholinate of lead, and the bilin remains undissolved. The filtered solution of bilin is evaporated to dryness; and to separate foreign matters, the mass is again dissolved in alcohol, filtered and evaporated to dryness. What remains is bilin. (Grundriss der Organischen chemie von Dr. F. Wöhler.)

Bilin is a translucent, colourless, inodorous mass, without crystallization, having a bitter and at the same time somewhat sweetish taste. It contains nitrogen, and is decomposed by heat, with the formation of ammoniacal products. Water and alcohol dissolve it in all proportions; it is insoluble in ether. Its solution in water is not precipitated by acids, chlorine or metallic salts. Bilin is a readily alterable substance; by boiling with caustic alkali, it is decomposed and resolved into cholic acid and ammonia. It is decomposed by acids into five different substances, namely ammonia, taurin, fellinic and cholinic acids, and dyslysin; a decomposition which may occur in the bile of the living body.

When bilin is dissolved and digested in dilute hydrochloric acid, an oily substance presents itself, consisting of bilin in combination with fellinic and cholinic acids, which by farther digestion changes into a resin-like mass, insoluble in water. The solution then contains sal ammoniac and taurin; while the resinous mass consists of fellinic and cholinic acids with dyslysin. The two former may be dissolved out of the resinous mass by cold alcohol.

Dyslysin remains undissolved in the last operation, as a resin-like mass. It dissolves, although with some difficulty, in boiling alcohol, and falls again, after evaporation and cooling, as a white earthy mass. It has not been further investigated.

Taurin, $C_4H_7NO_{10}$, discovered by Demarçay, is a neutral substance which crystallizes in colourless regular six-sided prisms terminated by four or six-sided pyramids, of a weak taste; and is fusible by heat without decomposition. It is soluble in fifteen and a half times its weight of water at 53°6 (12° centig.); insoluble in absolute alcohol. It is dissolved without decomposition by concentrated sulphuric and nitric acids, and gives no reactions with the ordinary reagents.

Taurin may be derived directly from unprepared bile, when the latter, after precipitation of its mucus by hydrochloric acid, is boiled for a long time with an excess of the same acid; the liquid is poured off from the precipitated resinous acids, concentrated by evaporation, mixed with alcohol and set aside. The taurin crystallizes out mixed with common salt; the former is purified by solution in boiling water and crystallization. Taurin is the only one of these products that has been analysed.

Cholic acid may be prepared directly from bile, by precipitating the latter with acetate of lead, boiling the filtered solution with caustic potash, so long as ammonia escapes, and then adding acetic acid. The cholic acid separates in large white flocks, which soon assume a crystalline appearance.

Cholic acid crystallizes in fine needles, which when pressed together form a mass of a silky lustre, of which the taste is at once sharp and sweet; it is fused by heat, and burns like a fat. It is sparingly soluble in water, highly soluble in alcohol. It forms salts, with alkalies, of a sweet taste.

Fellinic acid is contained, with bilin and cholinic acid, in the plaster-like lead compound formed in the preparation of bilin, and in the alcoholic solution of the resinous mass produced by the treatment of bilin by hydrochloric acid. Its separation from cholinic acid is effected by saturating the last mentioned alcoholic solution with dilute ammonia and concentrating by evaporation: the cholinate of ammonia is then deposited as a hard mass, while the fellinate of ammonia remains dissolved. The addition of hydrochloric acid throws down the fellinic acid in white flocks.

After being washed and dried, fellinic acid forms a white, earthy, inodorous and bitter mass which fuses without decomposition at 212°. In boiling water it undergoes fusion and dissolves to a small extent; in alcohol it dissolves easily and the solution has the bitter taste of bile; in ether it is also soluble. Its salts of alkaline bases are soluble both in water and alcohol, but insoluble in an excess of alkali, and then precipitated as a plastic plaster-like substance. The salts of lead and barytes, which are insoluble, have the same appearance. It enters into combination with bilin, and forms in union with it a compound acid, which should be named *bilifellinic acid.*

Cholinic acid is separated from its salt of ammonia lately mentioned, by hydrochloric acid, in the form of white flocks, and becomes by aggregation, on drying, an easily pulverised mass. It is readily fused by the heat of hot water, in which it is wholly insoluble; it dissolves easily in alcohol.

Biliverdin is separated from its compound with barytes, mentioned under bilin, by digestion in dilute hydrochloric acid which dissolves the barytes. The residue of biliverdin is purified by solution in alcohol and precipitation from the latter by water. It forms a brilliant, greenish brown tasteless mass, insoluble in water, dissolving easily in an alkali, and precipitated from that solution in green flocks by an acid. It dissolves of a fine green colour in hydrochloric acid, and of a red tint in acetic acid. This principle of bile contains no nitrogen. The biliverdin of the bile of the ox appears to be identical with the chlorophyl of plants. That of carnivorous animals is different, although it may contain the same matter in combination with another substance. Such a substance appears to be the principal constituent of the yellow matter forming the concretions, found in the ox, which from the beauty and permanence of its tint is much prized by painters. These gall stones dissolve in caustic potash of a greenish brown colour, giving a solution which when over-saturated with nitric acid, becomes first green, and rapidly in succession blue, violet and red, and finally yellow.

Cholesterin, $C_{37}H_{32}O$.—This is a crystallizable substance which may be dissolved out of inspissated bile, by ether; it is also a constituent of the brain and nerves. It is contained in largest proportion by the gall stones of the human subject, which generally consist of this substance combined with a portion of the yellow colouring matter of the bile. Cholesterin may be obtained by digesting these concretions in a solution of potash, by which the colouring matter is readily dissolved, and the cholesterin left white; or by dissolving them in boiling alcohol, in which the colouring matter is insoluble.

Cholesterin crystallizes from an alcoholic solution in colourless small plates, of a pearly lustre; is insoluble in water, tasteless, fuses at 278°.6 (137° centig.), and solidifies again in a crystalline condition. If strongly heated apart from air, it sublimes unchanged in a great measure, and condenses in plates. It is but sparingly soluble in cold alcohol; is not altered by caustic alkalies.

The bile appears to act as a stimulus to the intestinal canal generally and to assist in dividing the chyme into chyle and fecal matter, by combining with the latter.

Chyle.—This is the fluid absorbed by the lacteal vessels from the small intestines during the process of digestion. As drawn from the thoracic duct of a mammiferous animal, it is an opaque milky liquid, in which two kinds of globules are perceived by the microscope. This liquid has already a considerable resemblance to blood; it soon coagulates; the clot reddens in the air and contains fibrin. The serum which separates is composed, with the usual undetermined animal substances and salts, principally of albumen and fat, which last comes to the surface, and is what constitutes, without doubt, one of the two species of chyle-globules.

Excrements.—The excrements of man usually contain about 25 per cent of solid matter, which necessarily varies considerably with the nature of his food. Besides the indigestible residue of the food, it contains mucus, an undetermined extractive matter, fat, salts and the whole constituents of the bile, to which it owes its colour. From the incineration of 100 parts of dried excrements, 15 parts of ashes have been obtained, which were principally composed of the phosphates of lime and magnesia. The value of night soil as manure is ascribed chiefly to these salts, and salts of ammonia from the urine.

SECTION V.

LIQUIDS OF SEROUS AND MUCOUS SURFACES AND PURULENT MATTER.

Lymph.—The liquid which moistens the surface of cellular membrane is called lymph; it is chiefly water, but contains a sensible quantity of common salt and of albumen, and when concentrated a trace of alkali sufficient to affect test-paper.

The liquid secreted by serous membranes, such as the pericardium, pleura and peritoneum, resembles lymph, but contains so much as 7 or 8 per cent of albumen and salts, and is distinctly alkaline, from the presence of carbonate or albuminate of soda. The liquor amnios and fluid of hydatides are of the same composition. The water of dropsy contains in addition urea, and cholesterin suspended in fine plates. All these liquids become turbid or coagulate, when boiled, or upon the addition of nitric acid to them.

Mucus.—This is the liquid secreted by mucous surfaces, such as the nostrils. The mucus of the nostrils usually contains about 93 per cent of water, 5 per cent of mucus, with a trace of albumen and the usual salts. Mucus is insoluble in water, but imbibes it and swells up, so as to form a ropy liquid, as if it were dissolved. It shrinks up in concentrated acetic acid, and is not dissolved. When dry it is yellow. It dissolves in caustic alkali, and forms a thin liquid. Mucus contains nitrogen, but its composition is otherwise quite unknown.

Pus.—The matter secreted by an inflamed and ulcerated surface is named pus. From a healing sore it is a yellowish white liquid, of the consistence of cream, which consists of round opaque globules floating in a transparent liquid. It is insoluble in water, but may be diffused through it; on standing, the globules fall as a yellow sediment, and the supernatant liquid becomes clear and colourless.

Pus contains about 86 per cent of water, and 14 per cent of solid matter. It is coagulated by heat and by alcohol. There have been found, by analysis, in pus, two albuminous principles, several fatty bodies besides cholesterin, with the usual salts and undetermined extractive matters.

The matter of the corpuscles of pus considerably resembles the globulin of blood. They are soluble in acetic acid with the exception of an exceedingly minute nucleus. The serum of pus contains albumen and another substance in larger quantity, to which the name *pyin* is applied, of which the solution in water is precipitated by alcohol, tannin, acetic acid, and most completely by alum, but not by ferrocyanide of potassium; the precipitates are insoluble in an excess of the reagents.

From *mucus* pus is distinguished by its different external characters, by the different form and smaller size of its microscopic corpuscles, by its different relations to water, and particularly by its becoming with caustic alkali, thick slimy and gelatinous, and in acetic acid assuming the appearance of an emulsion, while mucus becomes thinner with an alkali, and with acetic acid coagulates as a flocky matter which unites into a thready mass.

SECTION VI.

BLOOD, MILK, URINE.

Blood.—The constitution of the blood has already been described under the principal constituents of the clot, fibrin, hematosin and globulin, and albumen the chief constituent of the liquid portion. It is always alkaline from a salt of soda, probably the carbonate.

The following table exhibits the results of two careful analyses of human blood by M. Lecanu. (Ann. de Chim. &c. xlviii. 308.)

	Human blood.	
Water.	780.145	785.590
Fibrin.	2.100	3.565
Colouring matter (hematosin and globulin).	133.000	119.626
Albumen.	65.090	69.415
Crystalline fatty matter. . . .	2.430	4.300
Oily matter.	1.310	2.270
Extractive matter soluble in water and alcohol.	1.790	1.920
Albumen combined with soda. . .	1.265	2.010

Chloride of sodium.	8.370	7.304
——— potassium.		
Carbonates		
Phosphates of potash and soda.		
Sulphates		
Carbonates of lime and magnesia.	2.100	1.414
Phosphates of lime, magnesia, and iron.		
Peroxide of iron.		
Loss.	2.400	2.586
	100.000	100.000

Milk.—The history of this fluid has been partly given under its characteristic constituents casein, milk-sugar, and the acids of butter. It contains from 10 to 13 per cent of solid matter, the rest is water. It is not coagulated by heat, but readily by all sour liquids and by rennet. When heated, a skin of coagulated casein forms on its surface. The butter of milk consists of margarine, oleine and butyrine (page 954).

Milk may be made to undergo the vinous fermentation, although very slowly, and only after it contains lactic acid; which acid probably converts the milk-sugar into grape-sugar before the fermentation occurs.

An excellent examination has been made by MM. O. Henry and A. Chevallier, of the comparative composition of woman's milk, the milk of the cow and ass, of which I subjoin the results. (Journal de Pharmacie XXV. 333 et 401.

	ORDINARY MILK.		
	Woman.	Ass.	Cow.
Cheese.	1.52	1.82	4.48
Butter.	3.55	0.11	3.13
Sugar of milk.	6.50	6.08	4.77
Salts (or mucous matter).	0.45	0.34	0.60
Water.	87.98	91.65	87.02
	100.00	100.00	100.00

Urine.—This fluid is secreted by the kidneys from the arterial blood. The average density of healthy human urine is

1.0125, but it occasionally rises to 1.030; it is acid from free lactic acid. On standing it deposits a slimy mucus, and after a time, when stale, becomes alkaline from the formation of carbonate of ammonia. The latter salt is produced from the urea, which is accompanied in urine by a minute quantity of a fermenting principle, which occasions this transformation. Urine in its usual condition contains from 7 to 8 per cent of solid matter, the rest is water. Its characteristic constituents are urea (page 993) and uric acid (page 1002); the former is free or in combination with lactic acid, the last in an unknown combination.

Besides its usual saline constituents, the urine may contain in solution various bodies drawn by the kidneys from the blood. Many salts, such as nitrate of potash, ferrocyanide of potassium, pass through the circulation and are thrown off by the urine unaltered; so also are the organic acids, tartaric, oxalic, &c. when free; but the salts with alkalies of the same acids appear in the state of carbonates, and render the urine alkaline.

M. Lecanu has obtained some valuable results respecting the proportions of these substances in the urine of man, as affected by age and sex, which he deduces from a series of 120 analyses of urine.

He found that the quantity of urea passed in twenty-four hours, is in grammes (1 gramme = 15.44 grains troy):

	Minimum	Mean	Maximum
By men. . .	23.155	28.0525	33.055
By women. . .	. 9.926	19.1165	28.307
By old men (84 to 86 years).	. 3.956	8.1105	19.116
By children of eight years.	10.478	13.4710	16.464
By children of four years.	. 3.710	4.5050	5.300

The quantity of uric acid discharged is, like the urea, sensibly the same for the same individual in equal times, but varies much in different individuals. This difference was found to be in the twenty-fours, 0.362 to 1.343 grammes in the male adults, 0.229 to 0.652 in the old men, 0.394 to 0.907 in the women, and 0.198 to 0.32 in the children. (Journ. de Pharmacie, XXV, 681 et 746).

The following analysis by Berzelius exhibits the composition of urine in its ordinary state, in 1000 parts:

Water.	933.00
Urea.	30.10
Uric acid.	1.00
Free lactic acid, lactate of ammonia, and animal matter not separable from them.	17.14
Mucus of the bladder.	0.32
Sulphate of potash.	3.71
Sulphate of soda.	3.16
Phosphate of soda.	2.94
Phosphate of ammonia.	1.65
Chloride of sodium.	4.45
Hydrochlorate of ammonia.	1.50
Earthy matters, with a trace of fluate of lime.	1.00
Siliceous earth.	0.03

URINARY CONCRETIONS.

There are several distinct species of urinary calculi.

1. *Xanthic oxide*, a very rare calculus, discovered by Dr. Marcet. It has a light brown or bright brown surface; its fracture is scaly, with a brown or deep flesh colour, and becoming resinous by friction. It is distinguished by being entirely soluble in caustic potash, and precipitated by carbonic acid. It is thrown down as a white precipitate, which agglutinates in drying, and forms a pale-yellow, hard mass, which acquires a waxy lustre by friction. It is soluble in alkaline carbonates; also in nitric acid without effervescence. Its composition is expressed by $C_5N_2H_2O_2$.

2. *Cystic oxide*, a rare calculus, discovered by Dr. Wollaston. It appears, when broken, to form a yellowish-white, confused crystalline mass, having a brilliant waxy lustre. It is distinguished by its solubility in caustic potash, from which it is deposited on the addition of acetic acid, in hexagonal plates. It is also soluble in ammonia. The mineral acids dissolve cystic oxide with ease, and form crystalline compounds with it. The compound with hydrochloric acid is

anhydrous, and contains 1 atom of cystic oxide and of the acid. The nitrate contains 2 atoms of water, one of which it loses at 105°. The solution of cystic oxide in an alkali or alkaline carbonate is decomposed by heat, ammonia first coming off, and then as the evaporation proceeds, a combustible gas, which smells like sulphuret of carbon. This calculus contains sulphur, and is represented by $C_6NH_6O_4S_2$ (Thaulow).

3. *Oxalate of lime, or mulberry calculus*, has a dark-coloured tuberculated surface, is very hard and compact, rarely large. It is easily distinguished by the circumstance that its powder does not dissolve in acetic acid; but after being heated on a spatula to low redness, in the flame of a spirit-lamp, it dissolves readily in that acid with effervescence, the oxalate of lime having been converted into carbonate. The composition of crystallized oxalate of lime is CaO,C_2O_3+2HO.

4. *Bone-earth calculus*; its surface is pale brown and quite smooth, as if it had been polished. It is compact, and when sawed through, appears very regularly laminated. It is distinguished by its powder dissolving in dilute nitric and hydrochloric acid, but not in acetic acid, nor in solution of caustic potash. It appears white and not easily fused before the blow-pipe. The composition of bone-earth is expressed by $8CaO,HO+3PO_5$.

2. *Ammoniaco-magnesian phosphate calculus* is composed of the phosphate of magnesia and ammonia, which precipitates in granular crystals when phosphoric acid is added to a mixed solution of a salt of magnesia and ammonia (page 508). It is white and less compact than the last, and sparking crystals of the salt are often perceptible in the mass. It emits ammonia when heated to 212°, is dissolved by cold acetic acid and precipitated again on neutralising the acid. It emits ammonia when digested in a solution of potash, but does not dissolve. It fuses into a white pearly globule by strong heat of the blow pipe. The composition of crystallized phosphate of magnesia and ammonia is $2MgO.NH_4O,PO_5+14HO$.

6. The *fusible calculus* is a mixture of the two last, is common in old and exhausted subjects, and often attains a large size. It is commonly white, rather friable and chalky; its fracture rugged and uneven, and surface dusty. It melts easily

before the blow pipe into a pearly globule. Part of it dissolves in acetic acid, the rest in hydrochloric acid.

7. The ***uric acid calculus*** is perhaps the most common. It is usually of an oval form, of a brownish or fawn colour and smooth surface, and composed of concentric layers round a central nucleus, which is often foreign matter. Consisting of volatile elements, like the first and second species, it is consumed before the blow pipe, leaving only a trace of white ash. The powder of this calculus is soluble in a dilute and warm solution of caustic potash, and on adding an acid, uric acid is precipitated as a white powder. It is dissolved with effervescence by nitric acid of the ordinary strength, and the solution when evaporated nearly to dryness, and treated with a drop of ammonia exhibits the beautiful pink colour of murexide (see uric acid, page 1003). The formula for uric acid is $C_{10}H_4N_4O_6$.

8. The *urate of ammonia* forms a comparatively rare calculus. It has the chemical properties of the last species, with the additional property of emitting ammonia when dissolved in a dilute and warm solution of caustic potash.

SECTION VIII.

SOLID PARTS OF ANIMALS.

Bones.—When bones are digested in very dilute hydrochloric acid, their earth is dissolved out, and an organic matter remains, consisting of cartilage, which retains the form of the bones. This matter when moist is flexible and elastic; by drying it shrivels up and becomes brittle, but remains translucent. It is entirely dissolved by boiling in water, and gives a solution of gelatin (page 1036). Water heated above 212°, under pressure, dissolves the cartilaginous matter entirely out of bones, and leaves the pure bone-earth.

When bones are distilled in a close vessel, they yield ammonia and oily volatile products, while the earth remains behind, black, from the presence of 8 or 10 per cent of charcoal, which in this divided state and associated with the earth, has a high decolourising power. It forms animal charcoal, bone or ivory black. Bones burn white, on the other hand, in an open fire, and leave the bone-earth. The phosphate of lime in bones is peculiar, it contains 8 proportions of lime to 3 of phosphoric acid, or $8CaO+3PO_5$; but it is undoubtedly a compound of two tribasic phosphates of lime, namely, $2CaO,HO,PO_5+2(3CaO,PO_5)$; containing 1 atom of water before calcination. The proportion between the earth and cartilage varies in different bones; the human scapula has been found to contain 54½, the temporal bone 63½ per cent of bone-earth. Human bones well dried are said to contain 11 per cent of carbonate of lime, which is three times the quantity in the bones of the ox. Fluoride of calcium is also found in bones, although not uniformly present according to Dr. Rees' observations. The salt in question occurs in fossil bones, and is contained in considerable quantity in the human bones found in Herculaneum. In weak or ricketty bones the proportion of bone earth has been found diminished by 14 per cent. M. Valentin finds, by the analysis of morbid osseous formations, that the callus and exostosis contain more carbonate of lime than the sound bone upon which they form, and that, on the contrary, the caries contains a quantity of carbonate of lime smaller by several per cent than the sound bone.

The *teeth* are composed of the same materials as bone, but contain less cartilage; usually about 64 per cent of phosphate of lime, about 6 per cent of carbonate of lime with carbonate of magnesia, and 28 per cent of cartilage. The *ivory* of the teeth contains no cartilage, about 88 per cent of phosphate of lime, with some fluoride of calcium, and 10 per cent of carbonate of lime, with magnesia. The antlers of deer have the same composition as bone.

Skin.—The cuticle or epidermis is a coating of horny matter (page 1039), without blood-vessels. The mucous membrane (*rete Malpighi*), between the cuticle and true skin, appears to consist of the matter of the epidermis not yet hardened. The *corium* or true skin is completely decomposed by digestion in boiling water, and yields a solution of gelatin (page 1036). The composition and peculiar characters of the organic matter in *nails*, *claws*, *hoofs*, *hair*, *wool*, and *feathers*, have already been described (pages 1041, 1042). All these substances contain, besides, from ½ to 2 per cent of bone-earth.

Human perspiration has an acid re-action, it is supposed from acetic acid, but from its observed effects upon the dyed colours of prints, it must occasionally be formic acid. Its fixed constituents amount to from ½ to 1½ per cent, and consist of an undetermined animal matter, sal ammoniac, lactate of ammonia, chloride of sodium, and the other usual salts.

Muscle.—The threads or fibres of muscle consist essentially of fibrin (page 1024), but in addition to fibrin, several other substances are present, of which the nature is very imperfectly known. Flesh strongly dried, leaves about 23 per cent of solid matter, the other 77 per cent are water. Of the dry mass, about 6 per cent dissolves in water. Water extracts from hashed meat, about 17 per cent of its weight. This extract of meat is partly soluble in alcohol and partly insoluble. It is a mixture of salts with several organic substances, of which the true nature is still very doubtful. These undetermined extractive matters occur also in urine and most of the animal fluids. To one of them, soluble in both water and alcohol, and the cause of the odour of cooked meat, the name *osmazome* has been applied, but the matter so named has not the characters of a pure substance.

The fibrin of all animals is similar, for it has been found by Liebig, that the flesh of the ox, the deer, the cod and pike do not differ in composition.

The composition of *ligaments, cartilage, tendons,* &c. has already been described (p. 1036).

Fat.—Human fat appears to contain no stearine, but only margarine (page 959), and oleine (page 965). *Tallow,* or the melted fat of oxen and sheep, on the other hand, consists chiefly of stearine (page 961), with a little oleine. It forms excellent hard *soaps;* in the preparation of which, the melted tallow is boiled with a solution of caustic soda, weak at first, but gradually increased in strength; the soap floats upon the alkaline liquor, in which it is insoluble, while the glycerine of the tallow, which has been replaced in combination with the stearic and oleic acids, by soda, is dissolved by the water. In the formation of the common *diachylon plaster,* 9 parts of olive oil and some water are boiled with 5 parts of levigated litharge; a compound of margaric and oleic acids with the oxide of lead results, which forms a plastic mass, and is an insoluble soap. *Hog's lard* contains more oleine than tallow, and is softer; it probably, like human fat, contains margarine, although stearine also is undoubtedly present.

Brain and nerves.—The substance of the brain has been examined by more than one chemist, but most recently by M. Fremy. The brain of man contains 7 parts of albumen, 5 parts of a fatty matter, and 80 parts of water. The albuminous portion, after being coagulated by heat, is insoluble in water, alcohol and ether. The fatty matter is what has principally occupied attention; besides portions of the ordinary fatty substances, it contains two peculiar acids and cholesterin:

1. *Cerebric acid* which when purified is white, and presents itself in crystalline grains. It dissolves without residue in boiling alcohol, is almost insoluble in cold ether, more soluble in boiling ether. It has the remarkable property of swelling up like starch in boiling water, but appears to be insoluble in that liquid. It enters into fusion at a high temperature, approaching closely that at which it is decomposed, and is combustible. It contains no sulphur, but some phosphorus. The result of its analysis by Fremy, is 66.7 per cent of carbon, 10.6 of hydrogen, 2.3 of nitrogen, 0.9 of phosphorus, 19.5 of oxygen.

2. *Oleophosphoric acid*, which is separated from the former acid, by its solubility in ether. It is still accompanied by oleine and cholesterin, which are withdrawn from it by alcohol and ether. This acid is of a viscid consistence, insoluble in cold alcohol, but dissolving easily in boiling alcohol; it is insoluble in ether. Placed in contact with potash, soda and ammonia, it immediately gives soapy compounds. It forms compounds insoluble in water with other bases. M. Fremy has observed a remarkable transformation of oleophosphoric acid. When boiled for a long time in water or alcohol, it gradually loses its viscidity and becomes a fluid oil, which is pure *oleine*; while the liquor contains phosphoric acid. This decomposition becomes very rapid, when the liquor is rendered slightly acid. Although M. Fremy's attempts to form this acid directly, by uniting oleine and phosphoric acid, were unsuccessful, he still deems it probable that this acid may consist of the elements in question, and be analogous to the compound of sulphuric acid and oleine or sulpholeic acid (page 968). It contains from 1.9 to 2 per cent of phosphorus, in the condition, it is thus represented, of phosphoric acid.

M. Fremy has given a process for extracting cholesterin (page 1048) from the brain, in considerable quantity.

The constituents of the brain of man, enumerated by Fremy, are: 1. Cerebric acid free or combined with soda, or with phosphate of lime. 2. Oleophosphoric acid free and combined with soda. 3. Oleine and margarine. 4. Minute quantities of oleic and margaric acids. 5. Cholesterin. 6. Water and an albuminous matter. These results are quite different from those previously obtained by M. Couerbe, whose method of investigation appears to have been defective.

Fremy found a considerable quantity of cerebral matter in the spinal marrow, and very appreciable quantities of it in certain nerves.

The eye.—The *scelerotica* is dissolved, like the corium, by long boiling with water, and gives a solution of gelatin; it is said to contain no fibrin. The *cornea* is composed of cartilaginous fibres, and therefore consists of chondrin; but it contains besides, a small quantity of fibrin or albumen. The *pigmentum nigrum* (page 1043) has considerable resemblance to hematosin. The *vitreous* and *aqueous humours* consist of water with about 1½ per cent of common salt, a little albumen and undetermined animal matter. The substance of the *crystalline lens* agrees in properties with the globulin of the blood, and may be represented as a compound of 15 atoms of protein with 1 atom of sulphur. When rubbed in pure water, the greater part of the crystalline dissolves; the solution is coagulated by heat, and forms a granular and not a coherent mass. The crystalline undergoes the same coagulation when put into hot water, into alcohol, or into an acid.

APPENDIX.

TABLE I.

For the conversion of degrees on the Centigrade thermometer into degrees of Fahrenheit's scale.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50°	—58°.0	— 9°	15°.8	32°	89°.6
—49	—56 .2	— 8	17 .6	33	91 .4
—48	—54 .4	— 7	19 .4	34	93 .2
—47	—52 .6	— 6	21 .2	35	95 .0
—46	—50 .8	— 5	23 .0	36	96 .8
—45	—49 .0	— 4	24 .8	37	98 .6
—44	—47 .2	— 3	26 .6	38	100 .4
—43	—45 .4	— 2	28 .4	39	102 .2
—42	—43 .6	— 1	30 .2	40	104 .0
—41	—41 .8	0	32 .0	41	105 .8
—40	—40 .0	+ 1	33 .8	42	107 .6
—39	—38 .2	2	35 .6	43	109 .4
—38	—36 .4	3	37 .4	44	111 .2
—37	—34 .6	4	39 .2	45	113 .0
—36	—32 .8	5	41 .0	46	114 .8
—35	—30 .0	6	42 .8	47	116 .6
—34	—29 .2	7	44 .6	48	118 ,4
—33	—27 .4	8	46 .4	49	120 .2
—32	—25 .6	9	48 .2	50	122 .0
—31	—23 .8	10	50 .0	51	123 .8
—30	—22 .0	11	51 .8	52	125 .6
—29	—20 .2	12	53 ,6	53	127 .4
—28	—18 .4	13	55 .4	54	129 .2
—27	—16 .6	14	57 .2	55	131 .0
—26	—14 .8	15	59 .0	56	132 .8
—25	—13 .0	16	60 .8	57	134 .6
—24	—11 .2	17	62 .6	58	136 .4
—23	— 9 .4	18	64 .4	59	138 .2
—22	— 7 .6	19	66 .2	60	140 .0
—21	— 5 .8	20	68 .0	61	141 .8
—20	— 4 .0	21	69 .8	62	143 .6
—19	— 2 .2	22	71 .6	63	145 .4
—18	— 0 .4	23	73 .4	64	147 .2
—17	+ 1 .4	24	75 .2	65	149 .0
—16	3 .2	25	77 .0	66	150 .8
—15	5 .0	26	78 .8	67	152 .6
—14	6 .8	27	80 .6	68	154 .4
—13	8 .6	28	82 .4	69	156 .2
—12	10 .4	29	84 .2	70	158 .0
—11	12 .2	30	86 .0	71	159 .8
—10	14 .0	31	87 .8	72	161 .6

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
73°	163°.4	121°	249°.8	169°	336°.2
74	165.2	122	251.6	170	338.0
75	167.0	123	253.4	171	339.8
76	168.8	124	255.2	172	341.6
77	170.6	125	257.0	173	343.4
78	172.4	126	258.8	174	345.2
79	174.2	127	260.6	175	347.0
80	176.0	128	262.4	176	348.8
81	177.8	129	264.2	177	350.6
82	179.6	130	266.0	178	352.4
83	181.4	131	267.8	179	354.2
84	183,2	132	269.6	180	356.0
85	185.0	133	271.4	181	357.8
86	186.8	134	273.2	182	359.6
87	188.6	135	275.0	183	361.4
88	190.4	136	276.8	184	363.2
89	192.2	137	278.6	185	365.0
90	194.0	138	280.4	186	366.8
91	195.8	139	282.2	187	368.6
92	197.6	140	284.0	188	370.4
93	199.4	141	285.8	189	372.2
94	201.2	142	287.6	190	374.0
95	203.0	143	289.4	191	375.8
96	204.8	144	291.2	192	377.6
97	206.6	145	293.0	193	379.4
98	208.4	146	294.8	194	381.2
99	210.2	147	296,6	195	383.0
100	212.0	148	298.4	196	384.8
101	213.8	149	300.2	197	386.6
102	215.6	150	302.0	198	388.4
103	217.4	151	303.8	199	390.2
104	219.2	152	305.6	200	392.0
105	221.0	153	307.4	201	393.8
106	222.8	154	309.2	202	395.6
107	224.6	155	311.0	203	397.4
108	226.4	156	312.8	204	399.2
109	228.2	157	314.6	205	401.0
110	230 0	158	316.4	206	402.8
111	231.8	159	318.2	207	404.6
112	233.6	160	320.0	208	406.4
113	235.4	161	321.8	209	408.2
114	237.2	162	323.6	210	410.0
115	239.0	163	325.4	211	411.8
116	240.8	164	327.2	212	413.6
117	242.6	165	329.0	213	415.4
118	244.4	166	330.8	214	417.2
119	246.2	167	332.6	215	419.0
120	248.0	168	334.4	216	420.8

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
217°	422°.6	252°	485°.6	287°	548°.6
218	424 .4	253	487 .4	288	550 .4
219	426 .2	254	489 .2	289	552 .2
220	428 .0	255	491 .0	290	554 .0
221	429 .8	256	492 .8	291	555 .8
222	431 .6	257	494 .6	292	557 .6
223	433 .4	258	496 .4	293	559 .4
224	435 .2	259	498 .2	294	561 .2
225	437 .0	260	500 .0	295	563 .0
226	438 .8	261	501 .8	296	564 .8
227	440 .6	262	503 .6	297	566 .6
228	442 .4	263	505 .4	298	568 .4
229	444 .2	264	507 .2	299	570 .2
230	446 .0	265	509 .0	300	572 .0
231	447 .8	266	510 .8	301	573 .8
232	449 .6	267	512 .6	302	575 .6
233	451 .4	268	514 .4	303	577 .4
234	453 .2	269	516 .2	304	579 .2
235	455 .0	270	518 .0	305	581 .0
236	456 .8	271	519 .8	306	582 .8
237	458 .6	272	521 .6	307	584 .6
238	460 .4	273	523 .4	308	586 .4
239	462 .2	274	525 .2	309	588 .2
240	464 .0	275	527 .0	310	590 .0
241	465 .8	276	528 .8	311	591 .8
242	467 .6	277	530 .6	312	593 .6
243	469 .4	278	532 .4	313	595 .4
244	471 .2	279	534 .2	314	597 .2
245	473 .0	280	536 .0	315	599 .0
246	474 .8	281	537 .8	316	600 .8
247	476 .6	282	539 .6	317	602 .6
248	478 .4	283	541 .4	318	604 .4
249	480 .2	284	543 .2	319	606 .2
250	482 .0	285	545 .0	320	608 .0
251	483 .8	286	546 .8		

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
73°	163°.4	121°	249°.8	169°	336°.2
74	165.2	122	251.6	170	338.0
75	167.0	123	253.4	171	339.8
76	168.8	124	255.2	172	341.6
77	170.6	125	257.0	173	343.4
78	172.4	126	258.8	174	345.2
79	174.2	127	260.6	175	347.0
80	176.0	128	262.4	176	348.8
81	177.8	129	264.2	177	350.6
82	179.6	130	266.0	178	352.4
83	181.4	131	267.8	179	354.2
84	183,2	132	269.6	180	356.0
85	185.0	133	271.4	181	357.8
86	186.8	134	273.2	182	359.6
87	188.6	135	275.0	183	361.4
88	190.4	136	276.8	184	363.2
89	192.2	137	278.6	185	365.0
90	194.0	138	280.4	186	366.8
91	195.8	139	282.2	187	368.6
92	197.6	140	284.0	188	370.4
93	199.4	141	285.8	189	372.2
94	201.2	142	287.6	190	374.0
95	203.0	143	289.4	191	375.8
96	204.8	144	291.2	192	377.6
97	206.6	145	293.0	193	379.4
98	208.4	146	294.8	194	381.2
99	210.2	147	296,6	195	383.0
100	212.0	148	298.4	196	384.8
101	213.8	149	300.2	197	386.6
102	215.6	150	302.0	198	388.4
103	217.4	151	303.8	199	390.2
104	219.2	152	305.6	200	392.0
105	221.0	153	307.4	201	393.8
106	222.8	154	309.2	202	395.6
107	224.6	155	311.0	203	397.4
108	226.4	156	312.8	204	399.2
109	228.2	157	314.6	205	401.0
110	230.0	158	316.4	206	402.8
111	231.8	159	318.2	207	404.6
112	233.6	160	320.0	208	406.4
113	235.4	161	321.8	209	408.2
114	237.2	162	323.6	210	410.0
115	239.0	163	325.4	211	411.8
116	240.8	164	327.2	212	413.6
117	242.6	165	329.0	213	415.4
118	244.4	166	330.8	214	417.2
119	246.2	167	332.6	215	419.0
120	248.0	168	334.4	216	420.8

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
217°	422°.6	252°	485°.6	287°	548°.6
218	424.4	253	487.4	288	550.4
219	426.2	254	489.2	289	552.2
220	428.0	255	491.0	290	554.0
221	429.8	256	492.8	291	555.8
222	431.6	257	494.6	292	557.6
223	433.4	258	496.4	293	559.4
224	435.2	259	498.2	294	561.2
225	437.0	260	500.0	295	563.0
226	438.8	261	501.8	296	564.8
227	440.6	262	503.6	297	566.6
228	442.4	263	505.4	298	568.4
229	444.2	264	507.2	299	570.2
230	446.0	265	509.0	300	572.0
231	447.8	266	510.8	301	573.8
232	449.6	267	512.6	302	575.6
233	451.4	268	514.4	303	577.4
234	453.2	269	516.2	304	579.2
235	455.0	270	518.0	305	581.0
236	456.8	271	519.8	306	582.8
237	458.6	272	521.6	307	584.6
238	460.4	273	523.4	308	586.4
239	462.2	274	525.2	309	588.2
240	464.0	275	527.0	310	590.0
241	465.8	276	528.8	311	591.8
242	467.6	277	530.6	312	593.6
243	469.4	278	532.4	313	595.4
244	471.2	279	534.2	314	597.2
245	473.0	280	536.0	315	599.0
246	474.8	281	537.8	316	600.8
247	476.6	282	539.6	317	602.6
248	478.4	283	541.4	318	604.4
249	480.2	284	543.2	319	606.2
250	482.0	285	545.0	320	608.0
251	483.8	286	546.8		

TABLE II.

TABLE of the elastic Force of Aqueous Vapour at different Temperatures, expressed in Inches of Mercury.

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
32° F.	0.200	0.200	80° F.	1.00	1.010	128°F.	4.11	
33	0.207		81	1.04		129	4.22	
34	0.214		82	1.07		130	4.34	4.366
35	0.221		83	1.10		131	4.47	
36	0.229		84	1.14		132	4.60	
37	0.237		85	1.17	1.170	133	4.73	
38	0.245		86	1.21		134	4.86	
39	0.254		87	1.24		135	5.00	5.070
40	0.263	0·250	88	1.28		136	5.14	
41	0.273		89	1.32		137	5.29	
42	0.283		90	1.36	1.360	138	5.44	
43	0.294		91	1.40		139	5.59	
44	0.305		92	1.44		140	5.74	5.770
45	0.316		93	1.48		141	5.90	
46	0.328		94	1 53		142	6.05	
47	0.339		95	1.58	1.640	143	6.21	
48	0.351		96	1.63		144	6.37	
49	0.363		97	1.68		145	6.53	6.600
50	0.375	0.360	98	1.74		146	6.70	
51	0.388		99	1.80		147	6.87	
52	0.401		100	1.86	1.860	148	7.05	
53	0.415		101	1.92		149	7.23	
54	0.429		102	1.98		150	7.42	7.530
55	0.443	0.416	103	2.04		151	7.61	
56	0.458		104	2.11		152	7.81	
57	0.474		105	2.18	2.100	153	8.01	
58	0.490		106	2.25		154	8.20	
59	0.507		107	2.32		155	8.40	8.500
60	0.524	0.516	108	2.39		156	8.60	
61	0 542		109	2.46		157	8.81	
62	0.560		110	2 53	2.456	158	9.02	
63	0.578		111	2.60		159	9.24	
64	0.597		112	2.68		160	9.46	9.600
65	0.616	0.630	113	2.76		161	9.68	
66	0.635		114	2.84		162	9.91	
67	0.655		115	2.92	2.820	163	10.15	
68	0.676		116	3.00		164	10.41	
69	0.698		117	3.08		165	10.68	10.800
70	0.721	0.726	118	3.16		166	10.96	
71	0.745		119	3 25		167	11.25	
72	0.770		120	3.33	2.300	168	11 54	
73	0.796		121	3.42		169	11.83	
74	0.823		122	3 50		170	12.13	12.050
75	0.851	0.860	123	3.59		171	12.43	
76	0.880		124	3.69		172	12.73	
77	0.910		125	3.79	3.830	173	13.02	
78	0.940		126	3.89		174	13.32	
79	0.971		127	4.00		175	13.62	13.550

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure		Dalton.	Ure.
176° F.	13.92		201°F	24.12		226° F.	38.89	40.100
177	14.22		202	24.61		227	39.59	
178	14.52		203	25.10		228	40.30	
179	14.83		204	25.61		229	41.02	
180	15.15	15.160	205	26.13	25.900	230	41.75	4310 0
181	15.50		206	26.66		231	42.49	
182	15.86		207	27.20		232	43.24	
183	16.23		208	27.74		233	44.00	
184	16.61		209	28.29		234	44.78	46.800
185	17.00	16.900	210	28.84	28.880	235	45.58	47.220
186	17.40		211	29.41		236	46.39	
187	17.80		212	30.00	30.000	237	47.20	
188	18.20		213	30.60		238	48.02	50.300
189	18.60		214	31.21		239	48.84	
190	19.00	19 000	215	31.83		240	49.67	51.700
191	19.42		216	32.46	33.400	241	50.50	
192	19.86		217	33.09		242	51.34	53.600
193	20.32		218	33.72		243	52.18	
194	20.77		219	34.35		244	53 03	
195	21.22	21.100	220	34.99	35.540	245	53.88	56.340
196	21.68		221	35.63	36.700	246	54.68	
197	22.13		222	36.25		247	55.54	
198	22.69		223	36.88		248	56.42	60.400
199	23.16		224	37.53		249	57.31	
200	23.64	23.600	225	38.20	39.110	250	58.21	61.900

TABLE III.

Dr. Ure's Table of the Quantity of Oil of Vitriol, of sp. gr. 1.8485, *and of Anhydrous Acid, in* 100 *Parts of dilute Sulphuric Acid, at different Densities.*

Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.
100	1.8485	81.54	66	1.5503	53.82	32	1.2334	26.09
99	1.8475	80.72	65	1.5390	53.00	31	1.2260	25.28
98	1.8460	79.90	64	1.5280	52.18	30	1.2184	24.46
97	1.8439	79.09	63	1.5170	51.37	29	1.2108	23 65
96	1.8410	78.28	62	1.5066	50.55	28	1.2032	22.83
95	1.8376	77.46	61	1.4960	49.74	27	1.1956	22.01
94	1.8336	76.65	60	1.4860	48.92	26	1.1876	21.20
93	1.8290	75.83	59	1.4760	48.11	25	1.1792	20.38
92	1.8233	75.02	58	1.4660	47.29	24	1.1706	19 57
91	1.8179	74.20	57	1.4560	46.48	23	1.1626	18.75
90	1 8115	73.39	56	1.4460	45.66	22	1.1549	17.94
89	1.8043	72 57	55	1.4360	44.85	21	1.1480	17.12
88	1.7962	71.75	54	1.4265	44.03	20	1.1410	16.31
87	1.7870	70.94	53	1.4170	43.22	19	1.1330	15.49
86	1.7774	70.12	52	1.4073	42.40	18	1.1246	14.68
85	1.7673	69.31	51	1.3977	41.58	17	1.1165	13.86
84	1.7570	68.49	50	1.3884	40.77	16	1.1090	13.05
83	1.7465	67.68	49	1.3788	39.95	15	1.1019	12.23
82	1.7360	66.86	48	1.3697	39.14	14	1.0953	11.41
81	1.7245	66 05	47	1.3612	38.32	13	1.0887	10.60
80	1.7120	65.23	46	1.3530	37.51	12	1.0809	9.78
79	1.6993	64.42	45	1.3440	36.69	11	1.0743	8.97
78	1.6870	63.60	44	1.3345	35.88	10	1.0682	8.15
77	1.6750	62.78	43	1.3255	35.06	9	1.0614	7.34
76	1.6630	61.97	42	1.3165	34.25	8	1.0544	6.52
75	1.6520	61.15	41	1.3080	33.43	7	1.0477	5.71
74	1.6415	60.34	40	1.2999	32.61	6	1.0405	4.89
73	1.6321	59.52	39	1.2913	31.80	5	1.0336	4.08
72	1.6204	58.71	38	1.2826	30.98	4	1.0268	3.26
71	1.6090	57.89	37	1.2740	30.17	3	1.0206	2.446
70	1.5975	57.08	36	1.2654	29.35	2	1.0140	1.63
69	1.5868	56.26	35	1.2572	28 54	1	1.0074	0.8154
68	1 5760	55.45	34	1.2490	27.72			
67	1.5648	54.63	33	1.2409	26.91			

TABLE IV.

Dr. Ure's Table of the Quantity of Real or Anhydrous Nitric Acid in 100 *Parts of Liquid Acid at different Densities.*

Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.
1.5000	79.700	1.3783	52.602	1.1895	26.301
1.4980	78.903	1.3732	51.805	1.1833	25.504
1.4960	78.106	1.3681	51.068	1.1770	24 707
1.4940	77.309	1.3630	50.211	1.1709	23.910
1.4910	76.512	1.3579	49 414	1.1648	23.113
1.4880	75.715	1.3529	48.617	1.1587	22.316
1.4850	74.918	1.3477	47.820	1.1526	21.519
1.4820	74.121	1.3427	47.023	1.1465	20.722
1.4790	73.324	1.3376	46.226	1.1403	19.925
1.4760	72.527	1.3323	45.429	1.1345	19.128
1.4730	71.730	1.3270	44.632	1.1286	18.331
1.4700	70.933	1.3216	43.835	1.1227	17.534
1.4670	70.136	1.3163	43.038	1.1168	16.737
1.4640	69.339	1.3110	42.241	1.1109	15.940
1.4600	68.542	1.3056	41.444	1.1051	15.143
1.4570	67.745	1.3001	40.647	1.0993	14.346
1.4530	66.948	1.2947	39.850	1.0935	13.549
1.4500	66.155	1.2887	39.053	1.0878	12.752
1.4460	65.354	1.2826	38.256	1.0821	11.955
1.4424	64.557	1.2765	37.459	1.0764	11.158
1.4385	63.760	1.2705	36.662	1.0708	10 361
1.4346	62.963	1.2644	35.865	1.0651	9.564
1.4306	62.166	1.2583	35.068	1.0595	8.767
1.4269	61.369	1.2523	34.271	1.0540	7.970
1.4228	60.572	1.2462	33.474	1.0485	7.173
1.4189	59.775	1.2402	32.677	1.0430	6.376
1.4147	58.978	1.2341	31.880	1.0375	5.579
1.4107	58.181	1.2277	31.083	1.0320	4.782
1.4065	57.384	1.2212	30.286	1.0267	3 985
1.4023	56.587	1.2148	29.489	1.0212	3.188
1.3978	55.790	1.2084	28.692	1.0159	2.391
1.3945	54.993	1.2019	27.895	1.0106	1.594
1.3882	54.196	1.1958	27.098	1.0053	0.797
1.3833	53.399				

TABLE V.

Table of M. Lowitz, showing the Quantity of absolute Alcohol in Spirits of different Specific Gravities.

100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.	
Alc.	Wat.	At 60°.	At 68°.	Alc.	Wat.	At 60°.	At 68°.	Alc.	Wat.	At 60°.	At 68°.
100	0	0.796	0.791	66	34	0.881	0.877	32	68	0.955	0.952
99	1	0.798	0.794	65	35	0.883	0.880	31	69	0.957	0.954
98	2	0.801	0.797	64	36	0.886	0.882	30	70	0.958	0.956
97	3	0.804	0.800	63	37	0.889	0.885	29	71	0.960	0.957
96	4	0.807	0.803	62	38	0.891	0.887	28	72	0.962	0.959
95	5	0.809	0.805	61	39	0.893	0.889	27	73	0 963	0.961
94	6	0.812	0.808	60	40	0.896	0.892	26	74	0.965	0.963
93	7	0.815	0.811	59	41	0.898	0.894	25	75	0.967	0.965
92	8	0.817	0.813	58	42	0.900	0.896	24	76	0.968	0.966
91	9	0.820	0.816	57	43	0.902	0.899	23	77	0.970	0.968
90	10	0.822	0.818	56	44	0.905	0.901	22	78	0.972	0.970
89	11	0.825	0.821	55	45	0.906	0.903	21	79	0.973	0.971
88	12	0.827	0.823	54	46	0.908	0.905	20	80	0.974	0.973
87	13	0.830	0 826	53	47	0.910	0.907	19	81	0.975	0.974
86	14	0.832	0.828	52	48	0.912	0.909	18	82	0.977	0.976
85	15	0.835	0.831	51	49	0.915	0.912	17	83	0.978	0.977
84	16	0.838	0.834	50	50	0.917	0.914	16	84	0.979	0.978
83	17	0.840	0.836	49	51	0.920	0.917	15	85	0.981	0.980
82	18	0.843	0.839	48	52	0.922	0.919	14	86	0.982	0.981
81	19	0.846	0.842	47	53	0.924	0.921	13	87	0 984	0.983
80	20	0.848	0.844	46	54	0.926	0.923	12	88	0.986	0.985
79	21	0.851	0.847	45	55	0.928	0 925	11	89	0.987	0.986
78	22	0.853	0.849	44	56	0.930	0.927	10	90	0.988	0.987
77	23	0.855	0.851	43	57	0.933	0.930	9	91	0.989	0.988
76	24	0.857	0.853	42	58	0.935	0.932	8	92	0.990	0.989
75	25	0.860	0.856	41	59	0.937	0.934	7	93	0.992	0.991
74	2	0.863	0.859	40	60	0.939	0.936	6	94	0.991	0.992
73	27	0.865	0.861	39	61	0.941	0.938	5	95		0.994
72	28	0.867	0.863	38	62	0.943	0.940	4	96		0.995
71	29	0.870	0.866	37	63	0.945	0.942	3	97		0 997
70	30	0.872	0.868	36	64	0.947	0.944	2	98		0.998
69	31	0.874	0.870	35	65	0.949	0 946	1	99		0.999
68	32	0.875	0.872	34	66	0.951	0.948	0	100		1.000
67	33	0.879	0.875	33	67	0.953	0.950				

TABLE VI.

Tables showing the Specific Gravity of Liquids, at the Temperature of 55° Fahr. corresponding to the Degrees of Beaumé's Hydrometer.

For Liquids lighter than Water.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10 =	1.000	17 =	.949	23 =	.909	29 =	.874	35 =	.842
11	.990	18	.942	24	.903	30	.867	36	.837
12	.985	19	.935	25	.897	31	.861	37	.832
13	977	20	.928	26	.892	32	.856	38	.827
14	.970	21	.922	27	.886	33	.852	39	.822
15	.963	22	.915	28	.880	34	.847	40	.817
16	.955								

For Liquids heavier than Water.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
0=	1.000	15=	1.114	30=	1.261	45=	1.455	60=	1.717
3	1.020	18	1.140	33	1.295	48	1.500	63	1.779
6	1.040	21	1.170	36	1.333	51	1.547	66	1.848
9	1.064	24	1.200	39	1.373	54	1.594	69	1.920
12	1.089	27	1.230	42	1.414	57	1.659	72	2.000

TABLE VII.

TABLES FOR REFERENCE IN QUALITATIVE ANALYSIS.

I. GASES.

Distinctive properties of oxygen, nitrogen, protoxide of nitrogen, deutoxide of nitrogen, hydrogen, carbonic oxide and carbonic acid.

	GASES.	
Soluble in water.	Carbonic acid	Solution disturbs lime-water.
	Protoxide of nitrogen	Does not.
Support combustion	Oxygen	
	Protoxide of nitrogen	
Combustible	Carbonic oxide	Product of combustion disturbs lime-water.
	Hydrogen	Does not.
Extinguish combustion	Deutoxide of nitrogen	Forms brown fumes with oxygen.
	Nitrogen	Does not.

II. ACIDS.

Distinctive properties of certain acids, in combination.

	ACIDS.		
Precipitated by chloride of barium	Sulphuric		Precipitate not dissolved by nitric acid.
	Iodic		Precipitate dissolved by hydrochloric acid.
	Sulphurous		
	Phosphoric		
	Pyrophosphoric		
	Carbonic		
	Hyposulphurous		
Precipitated by nitrate of silver	Hydrochloric,	white	Precipitate not dissolved by nitric acid.
	Hydriodic,	yellow	
	Phosphoric	,,	Precipitate dissolved by nitric acid.
	Pyrophosphoric	white	
	Iodic	,,	
	Carbonic	,,	
	Sulphurous	,,	
	Hyposulphurous	,,	,, sulphur appears.

ACIDS.

Indicated by strong sulphuric acid.	Carbonic	Effervescence of a gas which renders lime-water turbid.
	Sulphurous	Effervescence: gas decomposes iodic acid.
	Hyposulphurous	Effervescence of sulphurous acid, and sulphur deposited.
	Hydriodic	Iodine liberated.
	Chloric	Peroxide of chlorine evolved, and liquid bleaches.

SPECIAL TESTS.

Hydriodic acid, by chlorine-water and starch.
Iodic acid, by sulphurous acid water and starch.
Sulphurous acid, by iodic acid and starch.
Nitric acid, by sulphate of indigo.
Hyposulphurous acid dissolves chloride of silver.
,, ,, is *not* precipitated by nitrate of strontian.

III. ALKALIES AND EARTHS.

Distinctive properties of potash, soda, ammonia, barytes, lime, strontian, magnesia and alumina, in their salts; the re-agents to be applied in succession as numbered.

RE-AGENTS.	
1° Carbonate of soda	Precipitates earths and not alkalies.
2° Oxalate of ammonia	Precipitates barytes, strontian and lime.
3° Diluted sulphate of soda	Precipitates barytes and strontian, but not lime.
4° Hyposulphite of soda	Precipitates barytes but not strontian.

SPECIAL TESTS.

Caustic potash evolves *ammonia*.
Tartaric acid in excess precipitates *potash*.
Bicarbonate of potash does not precipitate *magnesia*.
Caustic potash dissolves *alumina*.

IV. METALLIC OXIDES.

Distinctive properties of the oxides of certain of the metals proper, in their salts.

METALLIC OXIDES.	RE-AGENTS.			SPECIAL TESTS.
	Caustic potash.	Sulphuretted hydrogen; the metallic solutions being made strongly acid by a mineral acid.	Hydrosulphuret of ammonium.	
Protox. manganese	white, becoming brown	. .	flesh-colour	Chloride of lime gives manganese brown.
Protox. iron	white, becoming green	. .	black	Red prussiate of potash gives Prussian blue.
Perox. iron	ochry red	a little sulphur	black	Yellow prussiate of potash gives Prussian blue.
Oxide of zinc	white	. .	white	Ammonia re-dissolves oxide.
Oxide of copper	blue	black	brown black	Ammonia forms a deep blue solution.
Oxide of lead	white soluble in excess	black	black	Iodide of potassium gives yellow iodide.
Protoxide of tin	white, may dissolve in excess	brown black	brown black	Chloride of mercury, white and black.
Peroxide of tin	white, may dissolve in excess	light yellow	light yellow	Ignited oxide is not soluble in acids.
Oxide of chromium	dull green	. .	dull green oxide	Ditto.
Chromic acid	. .	sulphur and oxide of chromium	sulphur and oxide of chromium	Acetate of lead gives a yellow precipitate.

TABLE VIII.

SELECTED ATOMIC WEIGHTS, WITH THEIR LOGARITHMS, FOR THE CALCULATIONS OF ANALYSIS.

The numbers are the same as those given in the body of the work (from Berzelius), with the exception of carbon, which is always taken here at 75, *(Dumas), and nitrogen at* 175.6; *the last deduced by Dr. Clark from M. Dumas' recent determinations of the densities of nitrogen and oxygen.*

Name.	Symbol.	Atomic Weight.	Logarithm.
Ammonia	NH_3	213.13	2.32864
Antimony	Sb	1612.9	3.20761
—— (oxide of)	SbO_3	1912.9	3.28169
—— (sulphuret of)	SbS_3	2216.4	3.34565
Arsenic	As	940.1	2.973174
—— (sulphuret of)	AsS_3	1543.6	3.18854
—— (sulphuret of)	AsS_5	1945.9	3.28912
Arsenic acid	AsO_5	1440.1	3.15839
Arsenious acid	AsO_3	1240.1	3.09346
Barium	Ba	856.88	2.93292
—— (chloride of)	BaCl	1299.5	3.11378
Barytes	BaO	956.88	2.98086
—— (carbonate of)	BaO,CO_2	1231.9	3.09058
—— (phosphate of)	$2BaO,PO_5$	2806.1	3.44811
—— (sulphate of)	BaO,SO_3	1458.1	3.16379
Calcium, chloride of	CaCl	698.67	2.84427
Carbon	C	75.00	1.87506
Carbonic acid	CO_2	275.00	2.43933
Carbonic oxide	CO	175.00	2.24304
Copper	Cu	395.70	2.59737
—— (protoxide of)	CuO	495.70	2.69522
—— (suboxide of)	Cu_2O	891.39	2.95007
Hydrogen	H	12.48	1.09621
Iron	Fe	339.21	2.53047
—— (peroxide of)	Fe_2O_3	978.43	2.99053
—— (protoxide of)	FeO	439.21	2.64267
Lead	Pb	1294.5	3.11210
—— (carbonate of)	PbO,CO_2	1669.5	3.22259
—— (chloride of)	PbCl	1737.1	3.23983
—— (phosphate of)	$2PbO,PO_5$	3681.3	3.56600
—— (protoxide of)	PbO	1394.5	3.14442
—— (sulphate of)	PbO,SO_3	1895.7	3.27777
Lime	CaO	356.02	2.55147
—— (carbonate of)	CaO,CO_2	631.03	2.80004
—— (sulphate of)	CaO,SO_3	857.19	2.93308
Magnesia	MgO	258.35	2.41220
—— (sulphate of)	MgO,SO_3	759.52	2.88054
Manganese	Mn	345.90	2.53895
—— (protoxide of)	MnO	445.90	2.64924
—— (deutoxide of)	Mn_2O_3	991.80	2.99642
Mercury	Hg	1265.8	3.10236
—— (subchloride of)	$\frac{1}{2}(Hg_2Cl)$	1487.1	3.17234
—— (oxide of)	HgO	1365.8	3.13539
—— (suboxide of)	Hg_2O	2631.6	3.42022

Name.	Symbol.	Atomic Weight.	Logarithm.
Nitrogen	N	175.6	2.24452
Phosphoric acid	PO_5	892.31	2.95052
Phosphorous acid	PO_3	692.21	2.84030
Phosphorus	P	392.31	2.59363
Platinum	Pt	1233.3	3.09107
——— (ammonium chloride of)	$\left\{ \begin{matrix} Pt,Cl_2 + \\ NH_4Cl \end{matrix} \right\}$	2786.5	3.44506
——— (potassium chloride of)	$PtCl_2 + KCl$	3051·2	3.48447
Potash	KO	589·92	2.77079
——— (carbonate of)	KO,CO_2	864·93	2.93698
——— (sulphate of)	KO,SO_3	1091·1	3.03786
Potassium	K	489·92	2.69013
——— (chloride of)	KCl	932·57	2.96968
Silver	Ag	1351·6	3.13085
—— (chloride of)	AgCl	1794·3	3.25389
—— (oxide of)	AgO	1451.6	3.16185
	—2	2903·2	3.46288
	—3	4354.8	3.63897
	—4	5806·4	3.76391
	—5	7258.0	3.86082
Soda	NaO	390.90	2.59207
—— (carbonate of)	NaO,CO_2	665.91	2.82341
—— (sulphate of)	NaO,SO_3	892.07	2.95040
Sodium	Na	290.90	2.46374
——— (chloride of)	NaCl	733.55	2.86543
Strontian	SrO	647.29	2.81110
——— (carbonate of)	SrO,CO_2	922.30	2.96487
——— (sulphate of)	SrO,SO_3	1148.50	3.06013
Strontium, chloride of	SrCl	989.94	2.99561
Sulphur	S	201.17	2.30356
Sulphuric acid	SO_3	501.17	2.69998
Sulphurous acid	SO_2	401.17	2.60333
Tin	Sn	735.29	2.86645
—— (peroxide of)	SnO_2	935.29	2.97095
—— (protoxide of)	SnO	835.29	2.92184
Water	HO,	112.48	2.05107
	2	224.96	2.35210
	3	337.44	2.52820
	4	449.92	2.65314
	5	562.40	2.75005
	6	674.88	2.82923
	7	787.36	2.89618
	8	899.84	2.95417
	9	1012.3	3.00531
	10	1124.8	3.05107
	11	1237.3	3.09248
	12	1349.8	3.13027
	13	1462.2	3.16501
Zinc	Zn	403.23	2.60555
—— (oxide of)	ZnO 1	503.23	2.70177
	2	1006.5	3.00281
	3	1509.7	3.17889
	4	2012.9	3.30382

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